PHYSICO-CHEMICAL INTERACTIONS OF SURFACE TREATMENT ON PLASTIC FILMS USED IN FLEXIBLE PACKAGING

Thesis submitted by

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Doctor of Philosophy
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JADAVPUR UNIVERSITY

2023

JADAVPUR UNIVERSITY
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INDEX NO. D-7/ ISLM/32/18

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   II. **B. Das**, D. Chakrabarty, A. Mukherjee, C. Guha, and S. Bose, “Mechanical and Surface Properties of Corona Treated Titanium Dioxide embedded Opaque White low Density / linear low density polyethylene film,” *Polym. Eng. Sci.*, vol. 63, no. 2, pp. 546–561, 2023, doi: 10.1002/pen.26228.

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I Bidhan Das registered on 24/01/2018 do hereby declare that this thesis entitled **"Physico-Chemical Interactions of Surface Treatment on Plastic Films used in Flexible Packaging"** contains literature survey and original research work done by the undersigned candidate as part of Doctoral Studies.

All information in this thesis have been obtained and presented in accordance with existing academic rules and ethical conduct. I declare that, as required by these rules and conduct, I have fully cited and referred all materials and results that are not original to this work.

I also declare that I have checked this thesis as per the "Policy on Anti Plagiarism, Jadavpur University, 2019", and the level of similarity as checked by iThenticate software is 9%.

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Mr. Bidhan Das was born in Tufanganj Sub-division of Cooch Behar District, West Bengal in the year on 1976. He did his secondary and higher secondary schooling from Tufanganj Nripendra Narayan Memorial High School, Tufanganj, Cooch Behar District, West Bengal. He passed B.Sc. with Physics Honours from the Vidyasagar College, Calcutta University in 1997. Thereafter he joined Indian Institute of Packaging, Mumbai and completed Two Years Post Graduate Diploma in Packaging. After that he has completed M.Sc. in Physics from Sobhit University, Meerut and Environmental Sciences from the Nagaland Global Open University. Mr. Bidhan Das, presently working as a Deputy Director & Assistant Professor with Indian Institute of Packaging (IIP), Kolkata Centre and acting as the Head of the Eastern Regional Centre of Indian Institute of Packaging. He has worked with different organizations such as Emami Limited, Kolkata, Radha Madhav Corporation Ltd, Daman, Jhaveri Flexo India Limited, Silvassa, Dadra & Nagar Haveli, Roto Packing Materials Industry Company, Dubai, Akar Laminators Limited, Aurangabad etc. He is a professional member of Institute of Packaging Professionals (IoPP), USA since 2001. He is delivering lectures on Packaging as guest faculty in North Bengal University, Techno India College, Lady Brabourne College Kolkata, National Institute of Fashion Technology (NIFT) Kolkata and Shillong Campuses, and NSHM Knowledge Partner Kolkata. He has delivered more than 300 Lectures in different National and International Conferences / Seminars and Workshops organized by various Central and State Government Organizations, Government and Private Universities, Educational Institutions, Different Chamber of Commerce e.g. ICC, CII, FICCI, ASSOCHAM, BNCCI etc. He is a member in the Public Service Commission (PSC) of Government of West Bengal as a Subject Expert for Packaging in different Interview Boards. He is also providing voluntary service in the capacity of Managing Director in the West Bengal State Food Processing Corporation (WBSFPHDCL). He is member in various sectional committees of Bureau of Indian Standards (BIS) for formulation and revision of different Indian Standards. He is providing his services as the Examiner for the West Bengal State Council of Technical & Vocational Education and Skill Development, Govt. of West Bengal. He has around 23+ years of working experience in the field of Packaging in different capacities in India and abroad

Acknowledgment

I would like to express my gratitude to my advisors, Dr. Debabrata Chakraborty, Retired Professor, Department of Polymer Science & Technology, University of Calcutta, Dr. Chandan Guha, Professor, and Dr. Saswata Bose, Assistant Professor, Chemical Engineering Department, Jadavpur University, Kolkata for their guidance, inspiration and encouragement throughout my Ph.D program at Jadavpur University. I have benefitted from their profound knowledge, enormous and keen insight into the field of chemical engineering and polymer science. I am also indebted to them for giving me sufficient freedom to pursue my own ideas and develop myself as an independent researcher. It is my honour to have the opportunity of working under their supervision. I am very much thankful to all the Departmental Review Committee (DRC) members of Jadavpur University for selecting me for the Ph.D program, providing time to review my dissertation and for their valuable suggestions during the review.

I would like to extend my deepest thanks to Indian Institute of Packaging (IIP) administration including the Director and the Secretary to allow me to pursue my Ph.D at Jadavpur University, Kolkata. Furthermore, I would like to thank the former Director, Dr. (Prof) N.C. Saha, for his kind permission to use departmental facilities at IIP-Kolkata. I also want to thank all my colleagues at IIP-Kolkata. I am also thankful to M/S. A.B. Polypacks Private Limited, Kolkata for providing necessary assistance for fabrication of the LD/LLDPE films and conducting the trials in their factory for preparation of the samples for investigation. I also want to thank Dr. Sadhan Kumar Modak, Dr. Asitava Sur, Dr. Jagatbandhu Chakrabarti, Dr. Arup Mondal, Dr. Ayan Dey, Mr. Avik Mukherjee, Mr. Alok Basak, Mr. Anil P. Moule, Mr. Totan Das, Ms. Priyanka Gunin, Mr. Samudraneel Basu and others who have helped me in my work in many ways.

Finally, I would like to thank my family, my parents, Late Shri Biswanath Das and Smt. Jaba Rani Das, who instilled in me the values of life and responsibility, was my inspiration throughout the Ph.D program. I would also like to acknowledge the help and support of my wife Mrs. Debasree Das and my daughter, Ms. Samriddha Das without their love, support and help, it would have become difficult for me to complete my thesis successfully.

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Place: Kolkata Bidhan Das

Date: 06.12.2023

Dedicated to

My Family

CONTENTS

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: MATERIALS AND METHODS

CHAPTER 4: RESULTS AND DISCUSSIONS

APPENDIX

LIST OF ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
AFM	Atomic Force Microscopy
APT	Atmospheric Plasma Treatment
ASTM	American Society for Testing and Materials
atm	atmosphere
ATmaP™	Accelerated Thermo-Molecular Adhesion Process
BOPET	Biaxially Oriented Polyethylene Terephthalate
BOPP	Biaxially Oriented Polypropylene
bp	Boiling Point
BS	British Standards
BUR	Blow-Up Ratio
C	Celsius
CNTs	Carbon Nanotubes
CRFP	Carbon Reinforced Fibre Plastics
DC	Direct Current
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
EB	Elongation At Break
ECTFE	Ethylene-Chlorotrifluoroethylene
ESCA or XPS	Electron Spectroscopy For Chemical Analysis
ESR	Electron Spin Resonance
eV	Electron Volt
EV	Enhanced Velocity
FPA	Flexible Packaging Association
FTIR	Fourier Transform Infrared
FTS	Flame Treating Systems
gmf	Gram Force
g	Gram
GSM	Gram Per Square Metre

h	Hour(S) Or Height
HRTEM	High Resolution Transmission Electron Microscopy
Hz	Hertz
hν	Light
ICI	Imperial Chemical Industries
IEEC	Industrial Electronics Equipment Corporation
IEEE	Institute of Electrical and Electronics Engineers
IR	Infrared Spectroscopy
ISO	International Organisation for Standardisation
k	kilo
kcal	kilocalories
kW	Kilo Watt
L	Liter
LCB	Long Chain Branching
LDPE	Low Density Polyethylene
LIMM	Laser Intensity Modulated Method
LIP	Laser-Induced Pressure Pulse
LLDPE	Linear Low Density Polyethylene
LMWOM	Low Molecular Weight Oxidized Material
m	Meter
MAP	Modified Atmosphere Packaging
MET PET	Metalized Polyester
MFI	Melt Flow Index
min	Minute(S)
mol	Mole(S)
mol%	Mole Percent
mp	Melting Point
MW	Microwave
O.D.	Outer Diameter
O_2GTR	Oxygen Gas Transmission Rate
OTR	Oxygen Transmission Rate
PC	Polycarbonate

PCA	Principal Component Analysis
PE	Polyethylene
PET	Polyethylene Terephthalate
PET-G	Polyethylene Terephthalate Glycol
PMMA	Polymethylmethacrylate
PP	Polypropylene
PPS	Piezoelectric Pressure Step
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVA	Polyvinyl Alcohol
PVC	Polyvinyl Chloride
R	Alkyl Group
SEM	Scanning Electron Microscopy
SIMS	Second Ion Mass Spectroscopy
TEA	Tensile Energy Absorption
TSC	Thermally Stimulated Current
U.S.A	United states of America
UTM	Ultimate Tensile Machine
UV	Ultraviolet
Vis	Visual
VOC	Volatile organic compound
VUV	Vacuum Ultraviolet
w/v	Weight Per Volume
wt%	Percent By Weight
WVTR	Water Vapor Transmission Rate
XPS	X-ray Photoelectron Spectroscopy
λ	Wavelength
µ	Micro

LIST OF UNITS

SURFACE ENERGY	**(dynes/cm),(mJ/m^2)**
APPLIED WATTAGE	**(kW)**
KILOGRAMFORCE	**(kgf)**
WAVELENGTH	**(cm^{-1})**
ELECTRICAL ENERGY	**(eV)**
OXYGEN TRANSMISSION RATE (OTR)	**(cc/m^2 /day)**
WATER VAPOR TRANSMISSION RATE (WVTR)	**(g/m^2/ day)**
HEAT SEAL JOINT STRENGTH	**(kN/m)**
FILM THICKNESS	**(µm)**
PEEL ADHESION FORCE	**(kN/m)**
SCOTGH ADHESION STRENGTH	**(g/15mm)**

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

This dissertation is a comprehensive document that explains the urgent need of surface modification of the non polar,hydrophobic polyolefinic films by way of corona treatment, the most convenient and commercial technique of doing so. The surface energies of both the transparent and opaqueLD/LLDPE coextruded films were found to undergo an increase, the extent of which depends on the applied electrical load or voltage. The rate of enhancement was initially fast towards the low end of the range of voltage applied while it was comparatively low at higher wattage within the range of study.The change in surface energies of films is associated with modification of surface properties like scotch adhesion, coefficient of friction, heat-seal characteristics and surface morphology. However, the barrier properties of such treated films with respect to WVTR & OTR when compared with reference to untreated surface & amongst themselves were found to remain absolutely unaffected. The heat-seal joint strength was however greatly affected by the formation of a polar oxidized surface on the treated side. Amongst the different combinations of surfaces such as untreated/untreated, untreated/treated & treated/treated, the untreated/untreated showed the highest heat-seal joint strength and the treated/treated the lowest. The barrier properties of the films were hardly affected by such treatment. In case of identical film with white master batch of titanium dioxide (opaque films), the maximum surface energy was achieved at 3.0kW onlywith hardly any impact thereafter. The trend in changes of the heat seal joint strength followed the same pattern as that of transparent films. The mechanical, barrier, and aging characteristics of the films treated at different load were found to be independent of surface energy. The surface energy over the coating surface on the treated side hardly varied with colour, coating weight, and variation in the surface energies over the LD/LLDPE films which were corona treated at different electrical loads. The other surface features like roughness/coefficient of friction, the bulk mechanical properties and contact angle did not furnish any variation with respect to the original surface energies of the film.In case of film with corona treatment at different wattage and laminated with reverse printed (coloured surface being sandwiched) with 12µ PET films, the influence of surface charges of the PE films on the peel bond strength between the coloured PET film and the treated surface of the PE film was very little. However, for difference in the colour of PET film, some differences in the peel bond strength were observed. Among all the colours, the Magenta colour was found to exhibit the maximum peel bond strength.

Chapter 1:

INTRODUCTION

1. INTRODUCTION

1.1. Packaging

Packaging in today's world can be considered the index of growth and civilization and there is no sphere of life where its influence and necessity can be overestimated. With the advancement of polymer science, packaging technology is metamorphosing very fast and adding newer dimensions beyond the imagination and conception even a couple of years back. Not a single product, across their functionalities and usefulness, is left out from the revolutionary growth of this technology. Packaging primarily stands for preservation, protection, and performance. A proper selection of a packaging material adds desired physical attributes, makes awareness about the merits and demerits of its contents, provides guidelines for its use, and increases its aesthetic appeal. It is not an easy task to reach products to a far geographical location maintaining their integrity, shape, size, freshness, etc. particularly when depending on the geographical location, environment, natural treasures (crops, etc.), industries, and customer preferences notable variation in the form and style of packaging is evident. But packaging has broken all the boundaries and became a medium of mutual exchange bringing the nations closer and also in some cases established as undeclared ambassadors of specific nations. Classically, there are four important “P’s” of a marketing mix, which include Product, Price, Place, and Promotion. New age professionals consider “Packaging” as another novel “P” which is equally important for marketing and christened it as a “Silent Salesman” **[1]**.

Fig-1.1: The 5 “P”s of marketing [2]

The fact that the outward appearance of a prepackaged product is the package itself which draws the first attention of the takers and the first impression is known for creating a persistent effect in their mind, makes packaging a great marketing tool for any product.

But the utility of packaging is not only limited to serving as a marketing tool it serves many more important purposes. Some of its uses and functions are as follows:

- Protection: The basic and the most obvious function of packaging is the protection of the product. Physically, the package protects the goods from any sort of damage that may be caused due to various factors. It includes protection against impact, thrust, moisture, dust, temperature changes, etc.
- Information Transmission: Packaging along with labeling are considered to be an essential tool to convey information to the customer about the product. The set of information that packaging generally relays includes - directions for product use, storage instructions, ingredients, warnings, consumer care information, and any legal and obligatory warnings, etc. depending on the nature of the product and type of logistics.
- Convenience: Goods require transportation, distribution, storage, and warehousing during their journey from manufacturing to consumption. Packaging ensures proper and safe handling of goods that is most convenient for all stakeholders involved.
- Security: Packaging ensures that there is no tampering with the goods from the point of production till it reaches the end user. The package of a product plays a major role in securing/procuring goods from any part of the world. Quality packages reduce the risk of any kind of pilferage.

1.2. Classification of Packaging

Based on the function, packaging may be classified as Primary Packaging, Secondary Packaging, or Tertiary/Transport Packaging. Whilst, on the basis of the flexibility or rigidity of the packaging material, it may be broadly classified into three categories viz, rigid packaging, semi-rigid packaging and flexible packaging. Packaging materials are of many types’ namely flexible, rigid, metal, printed cartons, and glass along with caps & closures, labels, and others. About 22% of the total packaging market is explored by various flexible materials followed by rigid ones with 18% of share.

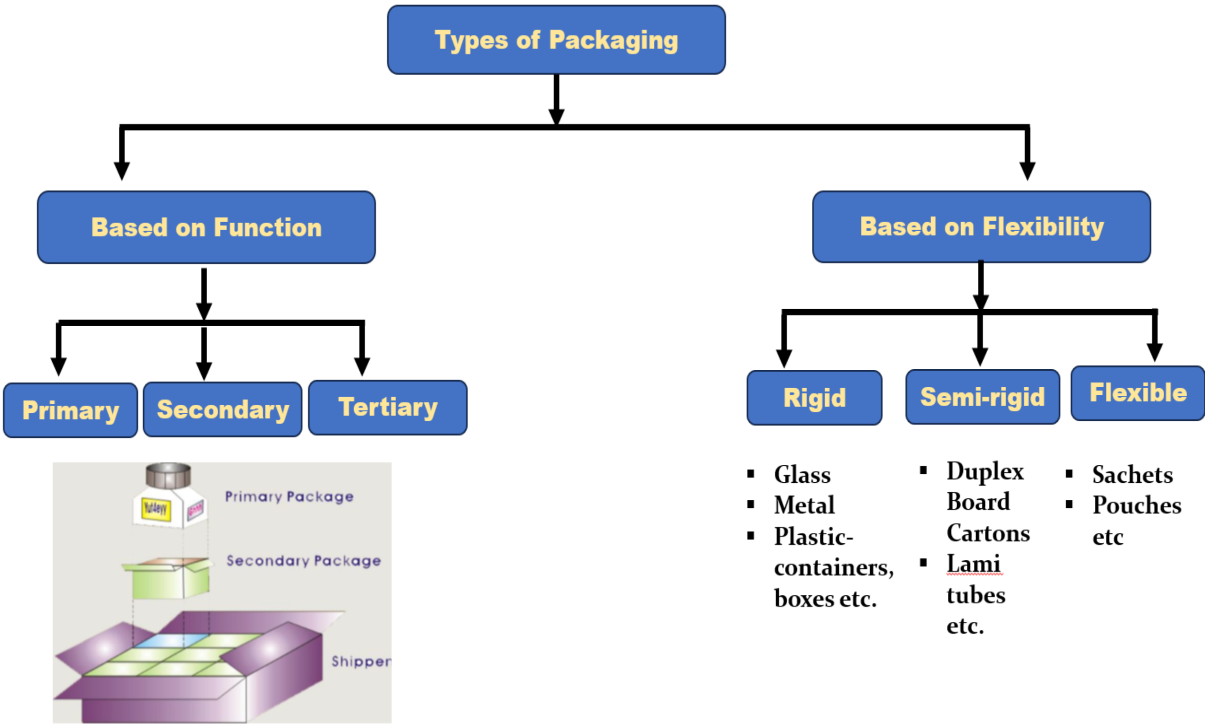


Fig-1.2: Types of Packaging [3,4,5]

The Indian packaging industry, historically, has witnessed an emergence in attractive investments in the last decade, most of which has been in the flexible packaging segment. The flexible packaging industry, though being predominantly an unorganized setup, has recently undergone consolidation to some extent, owing to the various acquisitions and mergers, which ultimately resulted in gaining the much-needed industrial upgradation in technology, scale, and skill development.

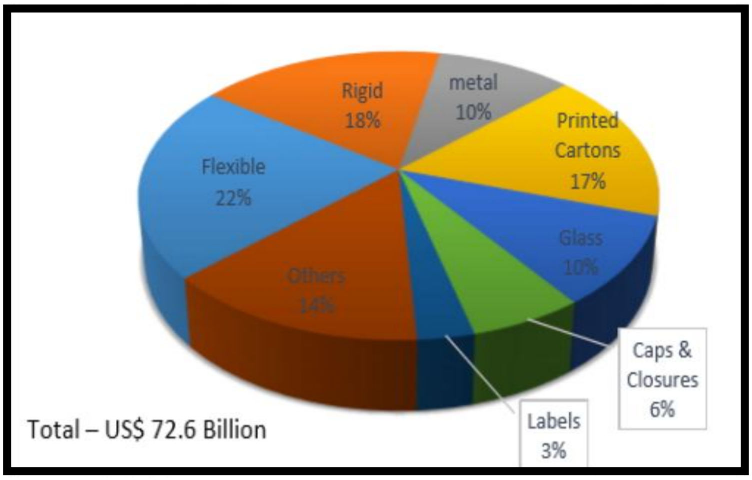


Fig-1.3: Market Share of Different types of Packaging [6,7]

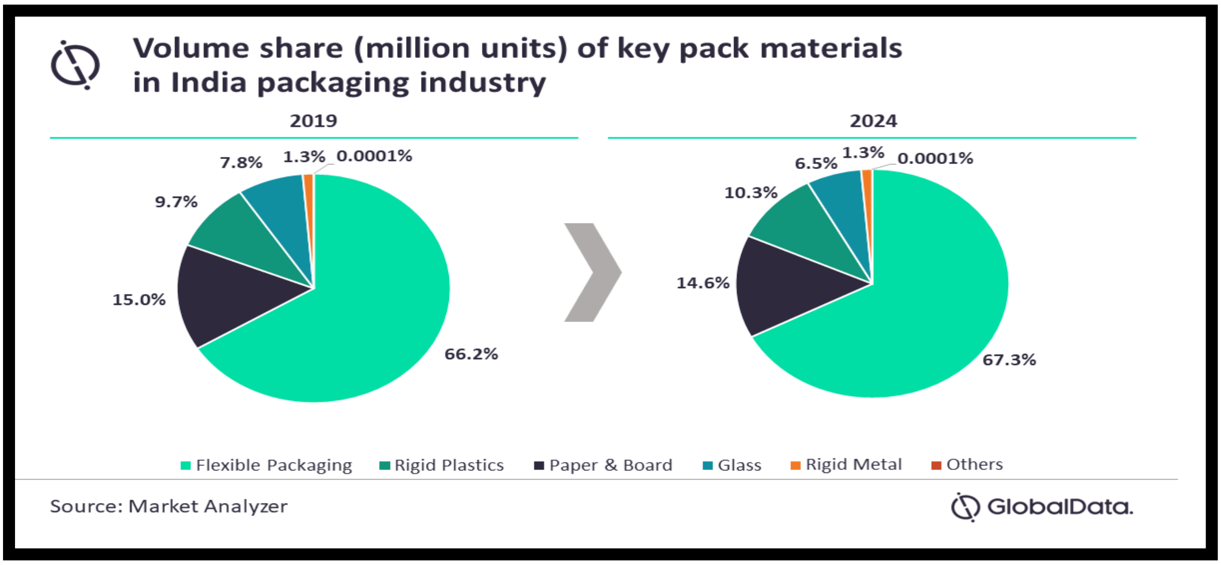


Fig-1.4: Volume share of major packaging materials [8]

1.3. Flexible Packaging

Flexible packaging has been gaining immense popularity over the years owing to various justified reasons. Advancements in technology concerning flexible packaging materials including all non-rigid materials, wraps, bags, pouches, envelopes, etc. make them far more suitable to consumer products in the current times, which were previously confined to rigid and hard materials. According to the reports of the Flexible Packaging Association (FPA) (probably 2016), the flexible packaging segment comprises 19% of the total U.S.A.'s packaging market. The United States of America earns about $170 billion in the world packaging market. This is mainly because of the following advantages of flexible packaging over the rigid ones:

- easy to store.
- convenient unpacking
- easy to close and reseal
- attractive shelf appeal.
- minimum usage of material, hence cost-effective.
- light weight
- better shipping characteristics
- e-commerce suitable

1.4. Polymers in Flexible Packaging

Advancements of high-tech plastics such as polyethylene (LDPE, LLDPE), polyethylene terephthalate (PET), polypropylene (PP), polyvinyl chloride (PVC), etc. with high durability, flexibility, and easy processability have been one of the main reasons behind the success of flexible packaging. Modern "end-of-life" recycling programs have been trending and propelling flexible packages more and more. As per reports, the flexible packaging industry sector is expected to grow by 3.3% each year to reach $269 billion worth by 2024 **[9]**. Polyethylene (PE) as a substrate remains the most widely used plastic by volume accounting for about 41% of overall flexible packaging material, now available in the market; followed by biaxially oriented polypropylene (BOPP) along with biaxially oriented polyethylene terephthalate (BOPET) **[10]**.

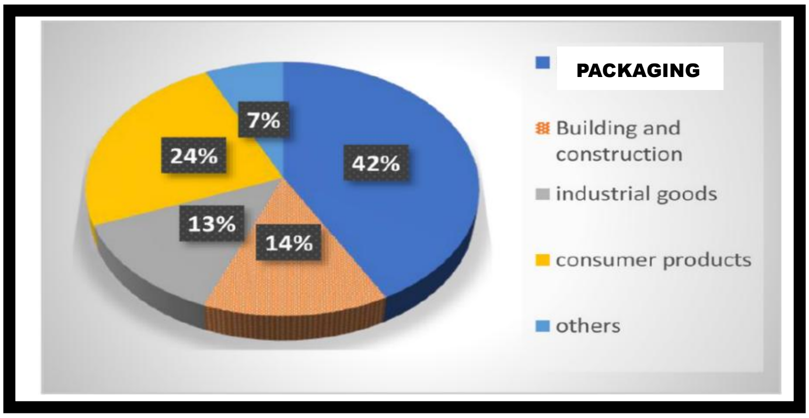


Fig-1.5: Use of plastics in different sectors [11,12,1]

Plastics with their inevitable characteristic to form thinner, lighter, more compact packaging films happen to serve appropriately in various ways, such as a single-layer material, coextruded films, laminations, or coatings. The availability and the unique processability of such thin films and foils have enabled the spurt of growth in flexible packaging to reach the stage where it is today.

Within the range of plastics available to date, polyethylene (PE) has been found to be the most extensively used one in the fabrication of plastic packaging films. Among the various grades of PE, low-density polyethylene (LDPE) and linear low density polyethylene (LLDPE) find major applications in packaging films.

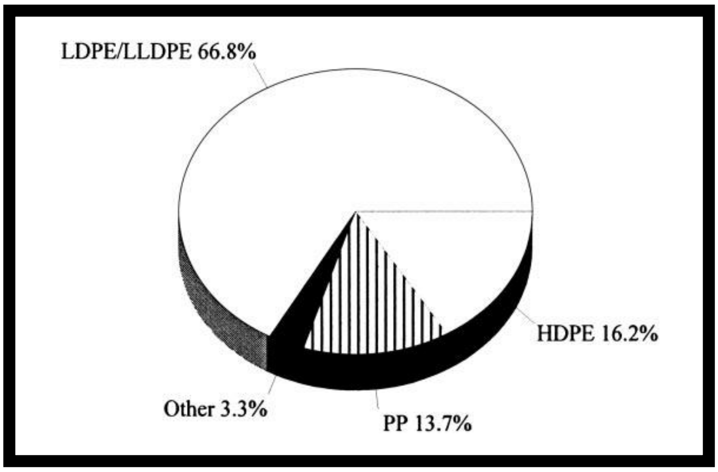


Fig-1.6: Percentages of different plastics used in flexible packaging. [13]

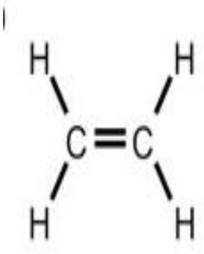
HDPE, PP, PS, PVC, and PET are among the rest of the plastics which also find their utilities in specific fields of packaging films.

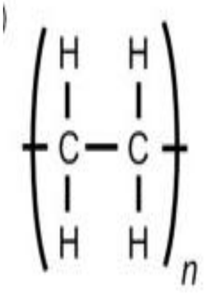
1.5. Polyethylenes

Polyethylene (PE), with advantageous characteristics like high flexibility, extraordinary toughness, and most significantly its cheap price has been one of the major polymers used in the manufacture of different flexible packaging specifications. The chemical structure of polyethylene consists only of carbon and hydrogen atoms, which makes the substance completely non-polar as the entire C and H atoms are covalently bonded mutually sharing their valence electrons.

It is a well-known fact that PE can be synthesized in various methods to give differently structured materials, possessing different densities, degrees of crystallinity, and molecular weight distribution. Further different olefinic simple molecules of co-monomer can be made to copolymerize at different percentages with ethylene to obtain a host of ethylenic polymers. Depending on the structure and properties, achieved by tailoring the processes of polymerization, the subclasses of generic polyethylenes include- LDPE, HDPE, and LLDPE.

Table-1.1: Comparing some features of different grades of PE [13]





Category	Density	Typical Chain Branching
Low Density Polyethylene (LDPE)	0.910 – 0.925 g/cm^3	
Linear Low Density Polyethylene (LLDPE)	0.919 – 0.925 g/cm^3	
Medium Density Polyethylene (MDPE)	0.926 – 0.940 g/cm^3	
High Density Polyethylene (HDPE)	0.941 – 0.965 g/cm^3	
Ultra High Molecular Weight Polyethylene (UHMWPE)	>0.966 g/cm^3	

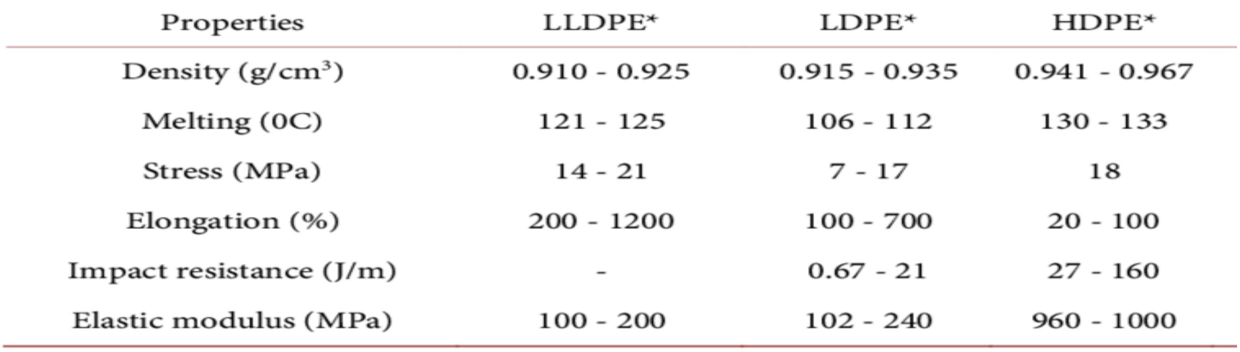
1.5.1. Low Density Polyethylene

This grade of polyethylene, developed by ICI back in the year 1930, was the primary manufactured and commercialized one. LDPE is synthesized via a free radical polymerization mechanism under high-pressure autoclave and tubular reactors. The polymer chains contain random and long chain branches, which happens to be a characteristic feature of the free radical method under stipulated high pressure. The presence of long chain branching (LCB) accounts for the easy processability of LDPE compared to that exhibited by the LLDPE grades. Furthermore, LCB imparts enhanced shear thinning character to the polymer melt that leads to a lower pressure developed during extrusion, a processing method to produce plastic films. Also, during extrusion, the LCB results in better stability of the blown film bubble and less neck-in. Generally, LDPE exhibits lower values of ultimate seal strength, dart impact resistance, as well as transverse direction tear strength compared to those of LLDPE. LDPE typically possesses a density between 0.910 and 0.925 g/cc. Being a homopolymer, LDPE's density and crystallinity could be controlled by tailoring the quantity of short-chain branching and its length, arising due to free radical polymerization. Some properties and uses of LDPE make them suitable for flexible packaging include- Sealing (tie resin) characteristic, adhesion or sealing property useful in extrusion coating over foil, paperboard etc, the opportunity of being used as a blending additive for LLDPE, used particularly in blown film preparation in order to enhance processibility as well as to increase bubble stability to give improved output and to substantially reduce haze.

1.5.2. Linear Low Density Polyethylene

As the name suggests, LLDPE, is comprised mainly of linear chains possessing very tiny or no branching. The tailor-made structural morphology of this polymer is done in the presence of an advanced coordination catalyst. The development of various catalysts resulted in the generation of LLDPE having desirable MWD (molecular weight distribution) and comonomer distribution. The density range of LLDPE varies from 0.910 to 0.925 g/cc. This could be controlled by the introduction of a comonomer during synthesis. Usually, three comonomers are used for this purpose which includes- butene, hexene, and octene. The size and concentration of comonomers govern the crystallinity and density of LLDPE, thereby affecting the overall properties. For instance, LLDPE films having butene as comonomers normally exhibit lower toughness than those with hexene or octene comonomers **[14,15]**. Commercially, LLDPEs are produced by three types of processes, which are the Gas phase-fluidized bed reactor process, Solution process, and Slurry loop process. The uses of LLDPE in the fields of flexible packaging are mostly governed by the following characteristics. They exhibit unique sealant properties, LLDPE may be used as components of tie resins, they behave as bulking layers and structural layers, etc.

Table-1.2: Comparing some physical properties of different HDPE, LDPE and LLDPE [16,17]



Properties	LLDPE*	LDPE*	HDPE*
Density (g/cm^3)	0.910 - 0.925	0.915 - 0.935	0.941 - 0.967
Melting (0C)	121 - 125	106 - 112	130 - 133
Stress (MPa)	14 - 21	7 - 17	18
Elongation (%)	200 - 1200	100 - 700	20 - 100
Impact resistance (J/m)	-	0.67 - 21	27 - 160
Elastic modulus (MPa)	100 - 200	102 - 240	960 - 1000

***Full forms already given in the "List of Abbreviations" section**

1.6. Surface of Polymers

Based on sources, polymers can be classified as natural and man-made. Natural polymers are derived from natural resources, which include- cellulose, chitosan, and collagen. These are extensively used in biomedical fields, owing to their high degradability [18,19]. The contributions made by various synthetic polymers such as PE, PP, PS, PU, etc have been immense, possessing key features of durability and wear-resistance. However, owing to the inherent, comparatively low surface energies, the applicability of non-polar polymers has been somewhat confined, thereby paving the way for various modified synthetic/secondary operational routes. For instance, some extent of hydrophilicity can be imparted to synthetic polymeric surfaces by incorporating polar functional groups.

Mainly polyolefinic (inert) surfaces such as those of PE, PP are considered to be non-absorbent substrates with regard to their holding capabilities of any ink formulation. Hence it requires surface treatment. PS, ABS, PVC, etc. are categorized as absorbent substrates, for which surface modification may not be necessitated. The two most commonly and widely used plastics in the field of packaging namely PE and PP are known to possess relatively a chemically inert and non-porous surface with low surface energy owing to their non-polar backbone structure. This fact is solely responsible for the difficulties encountered while printing or during the application of adhesives or any coating over such substrates **[20].**

It is a necessity to maneuver the surface chemistry of such substrates which could be done by creating a thin oxidized surface layer containing numerous roughness/etching/ irregularities at the micro level to overcome this problem. This could be accomplished/achieved by either electric corona discharge or by treatment with a gas flame, the former being preferred for films with lower thicknesses and especially for extruded cast and blown films. The various techniques of surface modification of polymers are extensively used in order to impart desirable surface properties enhancing efficient functionalities. Surface modification techniques not only enhance adhesion properties in polymers, but they also increase the scope of their uses in various fields including- biomedical applications textiles, water treatment, electronics, energy resources, microfluidics etc **[21-26]**. There are a number of ways/methods by which surface modifications can be accomplished. The commonly used strategies regulate the surface energies in polymers **[27]**, thereby improving its adhesion characteristics **[28]**, wettability, spreadability etc. Various surface treatment routes involve the action of chemicals, ionic substances, light, heat, radiations, etc. which all recondition the polymeric surface energies through the introduction of polar functional groups into the matrix **[29]**. The other pathway for achieving the same is by tailoring the surface undulations of a polymeric film or substrate by the process of mechanical or chemical ablation **[30].** The ablation process involves the action of dry or wet abrasive agents. Micro and nano-dimensional surface etchings are thereby produced by this technique imparting wetting and antifouling characteristics. Different strategies are adopted in order to modulate the surface roughness and energy of polymers which include physical methods, chemical etching, and some advanced non-invasive processes like UV irradiation, laser-induced patterning techniques, and corona/plasma treatment.

The properties of the interface between the adhesive/printing ink and the adherent are required to be analysed in order to deal with and solve the adhesion problems associated with the surface of any material. To achieve an acceptable level of adhesion, proper wetting of the polymeric surface is of high demand, as the formation of the adhesive-adherent assembly usually proceeds via a contact step between a solid and a liquid. The majority of surface treatment methods are mainly associated with the increment of surface energy of the polymer surfaces which in turn is related to the increase in their polarity **[31-36]**. As mentioned earlier, the wettability of the polymeric surface by any liquid is highly necessitated for establishing a strong adhesive bond, nevertheless, there are other various parameters that also play a vital role in this regard. Latest insights into the adhesion properties of polymers put emphasis on the influence of adsorption characteristics of the polymer as well as the polymer-liquid interfacial properties.

The liquids that mostly find application of adherence to polymeric surfaces are adhesives, paints, printing inks, coating melts, etc. In recent years, the techniques involving the engineering of polymeric surfaces have gained immense popularity in order to achieve workable adhesion strength.

1.7. Importance of Surface Treatment

Surface treatment is a process involving modification of the surface layer with different mechanical, physical, and chemical properties on the surface of the substrate. The purpose of surface treatment is to have the corrosion resistance, wear resistance, decoration or other special functional requirements of the product. In order to meet the requisite level of performance required for various applications, surface modification is adopted, bringing about morphological and energetic changes in plastics. Various methods are available for surface modification which include

1) physical processes, namely surface roughening and abrading;
2) liquid chemical processes, including acid etching; and
3) gas chemical processes including corona, and low-temperature plasma.

The selection of an appropriate method for a specific material is dependent on their surface characteristics. In some cases, plastic surface treatments and coatings may lead to the improvement of the performance in existing applications, as well as enable further use of them for new applications.

Surface treatments and coatings allow plastics to make inroads in a variety of applications, which were otherwise dominated by other materials like glass, ceramics, and metals. Moreover, in order to successfully achieve the required level of optical clarity, scratch and abrasion resistance, and exposure to weather, depending on the specific application, coating of the plastic is required at times **[37]**. The process of metallization of plastics facilitates the use of plastics replacing metal components along with the enhancement of the decorative opportunities for plastics.

The selection of the surface treatment and/or coating method is done for a given application depending on the properties aimed at and specifications, the substrate material over which it is to be applied, the end use and conditions in which the part will be applied, net cost associated with the process, and the ability to execute the treatment suiting the existing manufacturing processes. Such cases especially hold true for applications that involve the use of plastic as a replacement having a surface treatment or coating. For instance, adhesion tests, accelerated environmental exposure tests, chemical resistance, optical properties, scratch and abrasion resistance, stress-withstanding ability tests and many more are crucial to judge whether the application of surface-treated or coated plastics has been successful or not. Increasing environmental as well as safety considerations along with cost sensitivities are dictating the developments of modern surface treatment and coating technologies for plastics. As such, wet chemical treatment methods that are frequently associated with the significant use of harsh chemicals and concerns relating to chemical waste are prompting the gradual replacement by dry processes offering lower environmental issues. For instance, hexavalent chromium which is used in wet chemical treatment of plastics before metal plating, is known to be carcinogenic upon inhalation, thus, requiring the protection of personal protective equipment and controls to prevent exposure of workers. The use of hexavalent chromium in electronics has been prohibited by the European Union following the Restriction of Hazardous Substances Directive. Modern research focuses more on the use of environment-friendly chemicals for the purpose of pre-treatment of surfaces prior to metal plating **[38]**. For coating of plastics, radiation curing and water-based formulations are gradually being implemented aiming at a better environmental impact. Radiation curing requires lesser use of solvent, lower energy consumption, rapid curing times, and greater surface hardness and scratch resistance than conventional thermally cured coatings. In spite of their advantageous attributes, radiation-cured coatings are still employed for a meager fraction of the net coatings market **[39]**. In recent times, powder coating technologies have been employed over various plastics by means of a surface treatment that makes the surface of the substrates conductive, temporarily, by using a technique that generates no VOCs or hazardous by-products **[40].**

Modification

As already discussed before, non-polar polymers possess a very inert surface and, hence exhibit very poor wettability, spreadability, and adhesion characteristics. Surface modification techniques or surface treatment processes are commonly applied to plastic surfaces prior to coating, joining, or finishing operations, in order to remove contaminants, generate new surface reactive sites, and generate new surface functional groups facilitating the subsequent use of process chemicals. The low surface energy and surface smoothness of plastic usually create problems in the adhesion of a coating, a metalized layer, printing, decoration, or other finishing processes. Moreover, surface contaminants, such as additives, dust, and grit accumulate through static charges, which may again interfere with adhesion, finishing, or subsequent application of the plastic web or a part. Simple cleaning of the surface using mild solvents like isopropanol along with antistatic processing of the plastic part may be inadequate in terms of impurity removal and thus, a surface modification method is often applied. Various types of techniques have been adopted for modifying the surface of the plastic, at the submicron level, in order to increase the surface area and explore new bonding sites as well as increase surface energy, generate targeted chemical functional groups on the surface, and overall remove surface contaminants.

Broadly, the surface modification techniques may be classified into two following categories.

i) physical processes,

ii) liquid chemical surface modification, which include flame, plasma, and corona. Each of the types of surface modification process has its own advantages and limitations.

1.7.1. Physical Treatments

Physical surface treatment methods involve the modification of substrate surfaces through non-chemical routes. Physical surface treatments facilitate bonding to an adhesive or coating material by means of an increase in its surface area and by generating more sites for mechanical interlocking when applied on plastics. Conventionally, physical surface treatment methods include-

- surface roughening,
- adhesive abrading
- media blasting.

The extent of influence of the physical treatment is dependent on factors such as the type of plastic, the original surface quality, the abrading material, and various process parameters. The technique of surface roughening involves a simple process that can be carried out prior to the application of an adhesive or coating, intended for enhancing adhesion strength. It can be followed by operations such as degreasing by means of a solvent. The recommendations for the types of physical treatments to be used and the process of solvent cleaning depend on the polymer to be treated **[41]**. Surface roughening performed in the presence of an adhesive is normally referred to as “adhesive abrading”, which involves the abrasion of two surfaces along with adhesive coating prior to bonding and curing. The adhesive abrading process was found to increase the bond strengths of PTFE by nearly 700 % **[42]**. Media blasting is also a type of physical surface treatment method, involving the propulsion of small pelleted solid materials onto the surface of a plastic driven by a pressurized gas stream. Various propelling materials may be used for this purpose which includes sand, metallic shot, plastic pellets, crystals of dry ice, nutshells, and many others **[43]**. Although the physical surface treatments are all relatively simple and involve low cost, yet they are majorly ineffective for most types of plastics, coating, and adhesives. For such materials, chemical surface modification becomes useful.

1.7.2. Chemical (liquid) Treatments

The chemical processes of surface modification involve chemical reactions, driving the surface changes to produce the desired surface properties. The chemical methods of surface treatments are mostly performed in the liquid phase, as well as in the reactive gas or plasma state. When involving liquid phases, the processes are referred to as the wet chemical surface treatment methods. Wet chemical surface modification involves the exposure of the surface of a substrate to a chemical or to a mixture of chemicals in the liquid phase. A chemical reaction takes place between the chemicals and molecules on the surface of the substrate (such as plastic) to produce new surfacial functional groups. Liquid chemicals are capable of penetrating through pores more efficiently than other types of surface-modifying agents. Although, one shortfall of this method involves the use of a significant amount of chemicals, furthermore, high volumes of chemical waste are involved in wet chemical surface modification techniques, particularly when applied to large-scale production. In comparison, the reactive gas surface treatments are not associated with such drawbacks. The technique of acid etching of polymeric surfaces is carried out by the application of an acid in order to induce surface oxidation thereby resulting in an increase in the surface energy. Usually, this method is employed to enhance the bond strength between the polymer surface and an adhesive or any other coating material. Chromic acid is normally used for the purpose of acid etching of plastics, which is successful in introducing oxidized functional groups including hydroxyl (polar), carbonyl (polar), and carboxylic acid (polar), thereby enhancing the hydrophilicity of the material (polymeric) surface. Moreover, the process may even alter the surface morphology as well as lead to an increase in the surface area ultimately resulting in an increase in the number of sites for mechanical interlocking. The degree of oxidation along with the etch depth can be influenced by the nature of the plastic, the process temperature, and the etch time. For example, polypropylene (PP) responds by showing an increase only in etch depth on increasing etch time and temperature, on the other hand for polyethylene (PE), both degree of oxidation and etch depth vary proportionately with etch time **[44]**. Another report claimed that chromic acid etching on PP had led to an increase in the adhesion level of its surface on applying with an epoxy adhesive **[45]**. The other liquid surface treatments involve the use of comparatively milder chemicals such as the iodine treatment of nylon, which leads to an increase in the surface crystallinity of the polymer also enhancing its adhesion to a coating of metal. Both metallic Sodium and sodium compounds have been known to show efficiency in treating polymer surfaces for biomedical use, facilitating reduced inflammation and infection induced by synthetic materials used inside the body, exemplified by PP meshes **[46]**. Many liquid chemical surface treatments are associated with substantial drawbacks. One such drawback is that the wet chemical treatment involves the requirement of various additional processing steps including washing, rinsing, and drying. Additionally, wet processes produce a significant amount of waste, at times necessitating hazardous waste disposal. Various laws and regulations are compelling industries to drift away from the use of certain chemicals required in liquid surface treatments.

1.7.3. Reactive Gas Treatments

The Reactive gas processes, also sometimes referred to as the dry processes are associated with the generation of an energetic luminous gas containing high-energy neutral as well as charged species. When such processes involve the generation of matter in the plasma state, the process is termed plasma treatment method. The common types of reactive gas processes that are generally employed to modify the surfaces of plastics are as follows:

- flame treatments
- low-pressure non-equilibrium plasmas
- atmospheric non-equilibrium plasmas and
- corona discharges **[36-50].**

For the past few decades, the reactive gas processes have been employed to chemically modify the surfaces of plastic substrates. This plays a major role in increasing wettability, promoting adhesion to inks, coatings, and adhesives, and facilitating bringing about compatibility with other chemicals and contacting materials (in case of lamination), required to assist various subsequent processes (like printing, coating, laminating etc.) and in the final application of the product. These processes operate by modifying the surface of the substrate (plastic), yet keeping their bulk properties unaltered as mentioned earlier. Moreover, dry processes, typically do not produce any severe environmental impact (in terms of hazardous waste and emissions) in comparison to the liquid chemical processes. The surface treatment processes, which are considered to be the driest ones, would produce very fruitful results using only gases such as oxygen, nitrogen, or inert gases.

In reactive gas modification processes of plastic, the surfaces are subjected to the exposure of energetic species having energy greater than that possessed by the covalent bonds present in the organic polymer molecules. Such exposure to high-energy species leads to the removal of organic contaminants from the surface as well as results in surface cross-linking. It may also sometimes initiate reactions with the species present in the air forming new surface functional groups. However, overexposure may also lead to surface ablation and damage. Hence, depending on the given plastic and the final application, certain considerations are to be adopted including the type of treatments, applicable process conditions, and the probable limitations in connection with the purpose/utility of the final application. Moreover, various polymer additives present within the substrate may affect the surface treatability, the treated surface's stability as well as the compatibility between the treated surface and the final coating.

Chemical Effects of Reactive Gas Treatment on Polymeric Surfaces

The term "plasma" refers to different types of reactive gas discharges, including corona, flame, and low-temperature plasma. Low-temperature discharges consist of various reactive species such as ions, electrons, free radicals, metastable neutral species, ultraviolet (UV) and vacuum ultraviolet (VUV) photons, and ground-state neutrals. The surface experiences continuous bombardment by these plasma species, leading to reactions with the surface elements and resulting in changes in surface chemistry and characteristics when a plastic substrate is exposed to a plasma environment. Figure-1.7 illustrates the interactions between the plasma species and the plastic surface. Energy transfer from the plasma species to the polymer can lead to hydrogen or side-group species ablation, as well as chain scission, depending on the energy levels and the polymer's structure. Free radicals present in the reactive gas plasma can diffuse to the polymer surface and induce various chemical reactions, such as the abstraction of hydrogen or other side-group species, as well as the incorporation of chemical species into the polymer.

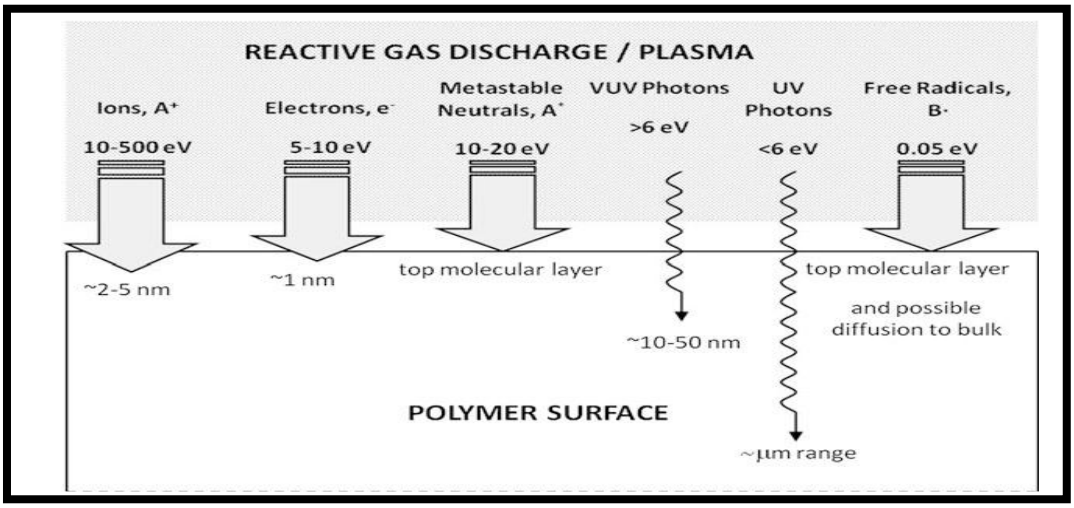


Fig-1.7: Interactions occurring between the highly energetic reactive gas species and the surface of plastic (polymer) [33]

Reactive gas treatment of polymer surfaces has four primary effects: surface cleaning, ablation or etching, surface chemical functionalization, and cross-linking. These effects are present to varying degrees depending on factors such as the specific process, energy and frequency used, gas chemistry, reactor design, and operating parameters **[47]**. Surface cleaning involves the removal of organic contaminants from the surface, including additives in the plastic, residues from previous processing steps, ambient air, or contact with other surfaces. Ablation and etching processes can remove surface material, increasing the surface area, creating reactive sites, and eliminating weak boundary layers that may hinder adhesion. Cross-linking and branching of surface macromolecules can strengthen the surface layers, enhancing their cohesion. Surface chemical functionalization involves modifying the surface's chemical structure to introduce new functional groups, which opens up possibilities for tailoring surface properties. Ablation and etching processes remove elements or small molecules from surface macromolecules, generating surface radicals. These radicals can react with reactive gas species in the plasma, leading to chemical functionalization reactions. The presence of free radicals in the reactive gas plasma allows them to diffuse to the polymer surface, triggering various chemical reactions such as hydrogen abstraction or incorporation of chemical species into the polymer. The extent and degree of these effects depend on the specific conditions of the reactive gas process, including process parameters, energy levels, gas chemistry, reactor design, and operating conditions.

In noble gas plasmas without the addition of reactive gases, the formation of new functionalities on the radical sites of polymer molecules is limited, and the significant consequence is the cross-linking with other polymer radicals. Plasma treatment leaves unreacted or residual surface free radicals on the polymer, which can incorporate oxygen, moisture, and nitrogen when exposed to the atmosphere. As a result, a stable, cross-linked top layer with primarily oxygen and some nitrogen functional groups can form on the surface in noble gas plasmas.

The susceptibility of the polymer to plasma exposure, the presence of additives on the surface, and the energy levels and duration of exposure determine the outcome of plasma treatment. It is important to note that plasma treatment can lead to polymer degradation and surface instability. Surface instability may arise from the degradation of the top layer of macromolecules into non-volatile, low molecular weight oxidized material (LMWOM), which can typically be removed from the polymer surface using a polar solvent **[51,52],[47].**

The presence of non-volatile, low molecular weight oxidized material (LMWOM) resulting from plasma treatment can lead to a weak and loosely bonded surface, negatively impacting surface stability and adhesion.

Oxidative degradation is a common phenomenon in most polymers, typically initiated by free radicals generated during plasma ablation reactions. This degradation process gives rise to peroxy and hydroperoxy intermediates. The formation of LMWOM on plasma-treated polymer surfaces can occur through the peroxy/hydroperoxy degradation pathway **[53]**. This pathway involves the initiation of a radical on the polymer surface, which then reacts with different plasma species to generate peroxy intermediates. The reactions leading to peroxy formation are depicted below.

Peroxy formation: $R^{\cdot} + O_2 \text{ (or } H_2O_2) \rightarrow ROO^{\cdot} \ (+H_2)$

Hydroperoxy formation: $ROO^{\cdot} + R_1H \rightarrow ROOH + R_1^{\cdot}$

$R^{\cdot} + HO_2^{\cdot} \rightarrow ROOH$

An alternative theory has been proposed regarding the formation of LMWOM on plasma-treated polymer surfaces. This theory suggests that the peroxy pathways, which involve the formation of peroxy intermediates, may be too slow to account for the significant LMWOM damage observed during plasma treatment. Instead, it is argued that reactions involving atomic oxygen and ozone are the main routes to the formation of LMWOM on polymer surfaces in plasma discharges. These atomic oxygen and ozone pathways can lead to the formation of alkoxy radicals, as shown in the reactions below.

Hydroperoxy decomposition: $ROOH \rightarrow RO^{\cdot} + {}^{\cdot}OH$

Alkoxy degradation: $R_1\text{-}C\text{-}C(O^{\cdot})\text{-}R_2 \rightarrow R_1\text{-}C^{\cdot} + R_2\text{-}C{=}O$

However, the exact reaction mechanisms that occur on the polymer surface during plasma treatment are still not fully understood. The complex nature of plasma-polymer interactions involves various plasma species such as ions, photons, electrons, atoms, and free radicals, those can induce chain scission, ablation of hydrogen or side-groups, and the generation of surface radicals. High-energy ions, in particular, have a greater tendency to cause chain scission and subsequent degradation. Plasma-activated surface macromolecules can undergo covalent bonding with surrounding species to create new functional groups, cross-link with other surface macromolecules, or further degrade into volatile etch products or LMWOM. However, the lack of selectivity in plasma treatment makes it challenging to optimize specific reaction pathways. The extent of surface degradation depends on the vulnerability of the polymer to the specific plasma environment, which is influenced by the chemical structure of the polymer. Factors such as the concentration and energy levels of plasma species, viz. oxygen, as well as the wavelengths and intensities of emitted VUV/UV photons, also play a role in determining the extent of degradation.

The precise mechanisms involved in the reaction processes occurring on the polymer surface during plasma treatment are still not fully understood. Figure-1.8 illustrates potential reaction pathways that can take place at the interface between the plasma and the polymer surface, resulting in various outcomes.

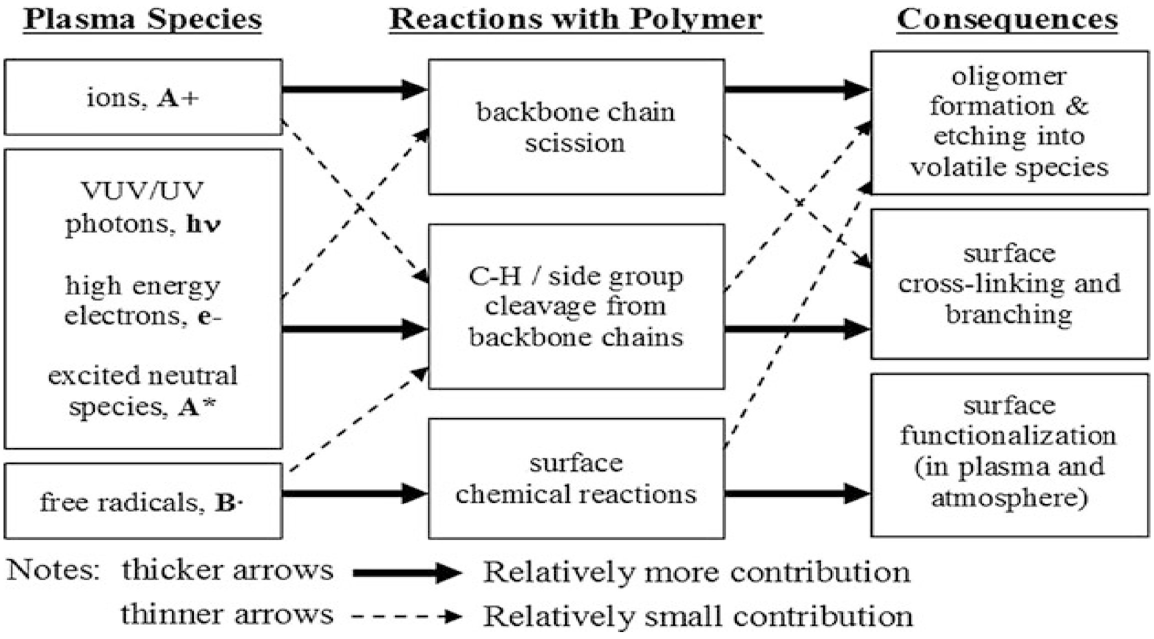


Fig-1.8: Possible mechanisms that can occur on a polymer surface exposed to a reactive gas discharge process. [33]

Plasma species, including ions, photons, electrons, atoms, and free radicals, can induce chain scission, hydrogen, or side-group ablation, leading to the formation of surface radicals. The plasma-activated surface macromolecules can undergo covalent bonding with surrounding species, generating new functional groups, cross-linking with other surface macromolecules, or undergoing further reactions that result in the formation of volatile etch products or LMWOM.

The susceptibility of organic polymers to plasma etching is influenced by the presence of oxygen in their structure, with oxygen enhancing the etching process **[54],[52]**. Conversely, polymers that contain aromatic rings exhibit a degree of resistance to surface etching **[56, 57].** Sensitivity to VUV/UV radiation in plasmas varies among organic polymers due to their unique photon absorption spectra, which in turn leads to different photochemical effects **[48]**. For instance, polymethylmethacrylate (PMMA) readily undergoes oxidative degradation in a plasma environment, while polystyrene (PS) demonstrates high stability against degradation **[56,57].** Silicon-containing polymers exhibit resistance to photodegradation and oxidative degradation but are prone to degradation in fluorine-containing plasmas due to the formation of stable and volatile Si-F compounds **[58].**

Plasma treatment introduces mobile functional groups on the polymer surface, which can undergo dynamic changes driven by interfacial tension and other surface forces. Langmuir's observations in the 1930s emphasized that the surface properties of solids are determined by the arrangement of surface functional groups rather than the bulk chemical configuration **[59].** As a result, polymers with mobile surface functionalities exhibit surface configuration alterations in response to different environmental conditions, enabling the surface to establish new equilibrium states that minimize interfacial tension **[60],[54],[52].** Over time, plasma-treated polymer surfaces stored in ambient air may undergo hydrophobic recovery, resulting in a loss of wettability. This recovery indicates a decrease in surface hydrophilicity due to surface configuration changes. However, studies have shown that prolonged hydrophobic recovery can be reversed by immersing the treated sample in water for a certain period **[52].** This reversal suggests that the hydrophilic surface moieties, generated by plasma treatment, rearrange toward the polymer surface when the surrounding conditions undergo transition from air to water, ultimately restoring the surface's wettability.

1.7.4. Flame Treatment

Flame treatment is a surface modification technique that involves applying a flame generated by burning gases like methane or propane to a substrate's surface. This process induces surface oxidation, leading to increased surface energy and wettability, which improves adhesion and printability. Flame treatment was first utilized in the 1950s, with one of its early applications being the enhancement of printability for low-density polyethylene (LDPE) **[58].** Compared to corona treatment, flame treatment offers several advantages, including uniform treatment, a smoother post-treatment surface, and longer-lasting surface stability. Unlike corona treatment, flame treatment primarily oxidizes the surface to depths of only 5-10 nm, while corona treatment can penetrate the plastic to much greater depths **[49].** A photograph of a flame treatment setup attached to a robot for treating three-dimensional parts is depicted in figure-1.9.

The adhesion improvement achieved through flame treatment is attributed to the increased surface energy of polymers resulting from surface oxidation. This treatment introduces new polar functional groups. For polyolefins, flame treatment can introduce approximately 5-15% oxygen to the surface **[58]**.

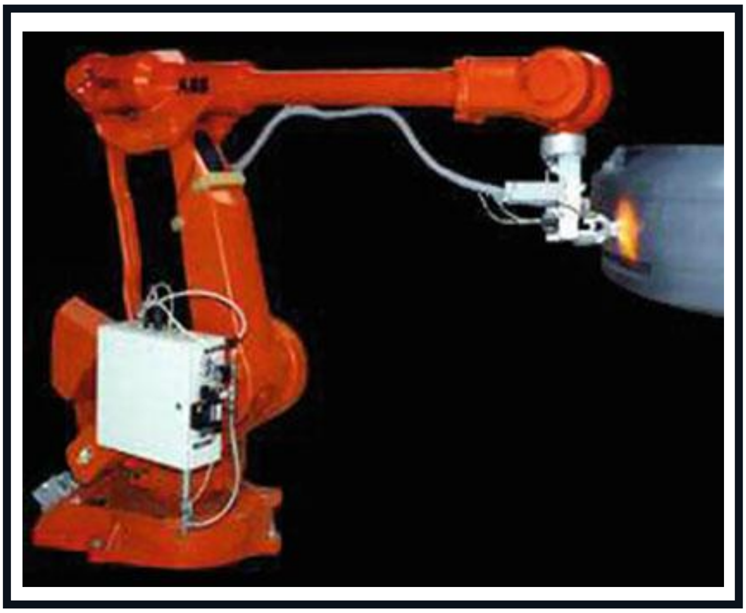


Fig-1.9: Image of flame treatment attached to robot courtesy of FTS Technologies

The chemical processes involved in flame treatment are believed to commence with hydrogen abstraction, leading to the formation of surface radicals. These radicals then react with oxygen atoms and molecules, giving rise to a variety of functional groups through interactions with other molecules in the flame plasma or on the polymer surface **[51].**

The primary exothermic reaction occurring during methane combustion in the flame plasma discharge can be represented as follows:

$$\mathbf{CH_4 + 2O_2 \rightarrow CO_2 + H_2O \text{ in the presence of } N_2}$$

The enhanced adhesion in flame treatment is attributed to increased surface energy, achieved through surface oxidation. This process introduces new polar functional groups, including hydroxyl, carbonyl, carboxyl, and nitrogen groups **[49].** For polyolefins, flame treatment can introduce oxygen to the surface, ranging from 5% to 15%. The chemical mechanisms involve the initial abstraction of hydrogen, leading to the formation of surface radicals, which then react with oxygen atoms and molecules. These surface radicals can further react with other species in the flame plasma or the polymer surface, resulting in the formation of various functional groups.

Flame plasmas also contain reactive side products and species generated during combustion, such as ethers, esters, carbonyls, carboxyls, and hydroxyls **[49].** These species can interact with the polymer surface during treatment, contributing to the formation of new surface functional groups. Additionally, specific chemicals can be introduced to the plastic surface during treatment to add desired functional groups. Notably, technologies like ATmaP™ (Accelerated thermo-molecular adhesion process) have demonstrated superior performance in meeting specific requirements, such as improving the painting process of automotive parts **[60].**

The effects of flame treatment are influenced by factors such as equipment design, operational parameters, and the characteristics of the substrate polymer surface. Operational parameters, including flame temperature, air/fuel stoichiometric ratio, gas flow rate, power density, air gap distance, and flame size and shape, determine the level of treatment. The design of the burner, such as ribbon burners or enhanced velocity (EV) burners, also plays a role in controlling thermal output, flame temperature, and geometry. These factors collectively affect the surface energy, adhesion, and treatment outcomes of flame plasma treatment.

1.7.5. Plasma Treatment

Plasma surface modification enables precise and controlled surface treatments without causing significant damage to the polymer surface. This method utilizes low-temperature plasma discharges to chemically modify the polymer surface through surface functionalization using reactive gas plasmas or surface crosslinking, including the CASING effect **[54],[51].** During plasma treatment, surface free radicals are generated, which can react with both the surrounding polymer molecules and the plasma species. Any remaining radicals can be quenched by oxygen, moisture, and nitrogen from the ambient air when exposed to the atmosphere.

There are various types of plasma processes used for plastic surface modification, distinguished by factors such as pressure, electrode configuration, power, energy etc. Low-pressure plasma processes are performed in vacuum chambers and can be conducted in batch or semi-batch continuous modes. On the other hand, atmospheric pressure plasma processes are conducted without the need for expensive vacuum equipment or chambers and can be easily integrated into existing plastic processing lines. The power configuration can be either direct current or alternating current, with frequencies ranging from kHz to microwave (MW). Higher frequencies lead to greater plasma ionization, although caution must be exercised with high-frequency microwave operation to avoid heat-related damage to the plastic. The choice of electrode configuration, such as capacitive or inductive coupling, and the overall chamber geometry also influence the effectiveness of the treatment.

Plasma surface modification offers superior alternative to corona treatment. Low-pressure processes offer advantages such as precise control, low gas flow rates, and uniform surface treatment. They come with certain limitations, including restricted part size and shape due to chamber constraints, high capital investment costs, and maintenance requirements extra equipments. While, atmospheric pressure plasma processes offer cost savings and can be seamlessly integrated into existing manufacturing lines. However, it is important to note that not all outcomes achievable with low-pressure plasma processes can be replicated using atmospheric plasma, and careful consideration is necessary when selecting the appropriate process. Overall, plasma surface modification provides a versatile and effective method for enhancing the properties of polymer surfaces, with the ability to create new functional groups and improve adhesion **[47].**

1.7.6. Corona Treatment

“Corona”- the term is usually used to characterize the condition of a gas (generally air), kept between electrodes. This typically involves a sharp point or wire electrode and a plate or cylinder electrode. The high electric field near the sharp electrode ionizes the normally insulating air, causing ions to be attracted toward the low-field electrode. Air, or any other common gas, is a good electrical insulator under normal conditions but becomes ionized by the influence of a strong electric field, thereby conducting electricity. As such there occurs a sudden electrical discharge between two electrodes, normally developing into an arc or a spark. Under such conditions, if a solid film is kept between the electrodes, the conductive path is disrupted temporarily. Such a condition produces a relatively cooler, diffused, soft glow in between the electrodes, instead of producing a hot localized arc. The bluish, soft discharge of the air under normal atmospheric pressure is called corona.

The onset of corona discharge depends on the presence of free electrons that can initiate an avalanche effect, leading to gas ionization. Electrons are effective at ionizing the gas because they transfer their energy from the electric field to gas molecules upon impact. The mechanism of corona production initiates with some stray electrons being present within the gas contained between electrodes due to cosmic rays or any other background radiation. On applying a high voltage, a strong electric field is developed, thereby accelerating the electrons and channelizing them towards the positive electrode. The electrons continue to strike gas molecules throughout their entire path. These electrons, hitting the molecules may knock out an orbital electron from there, generating a positive ion, while consequently, another electron may strike other molecules. The impacting electron forces an orbiting electron to a higher energy level, being relatively unstable, thus creating an excited molecule.

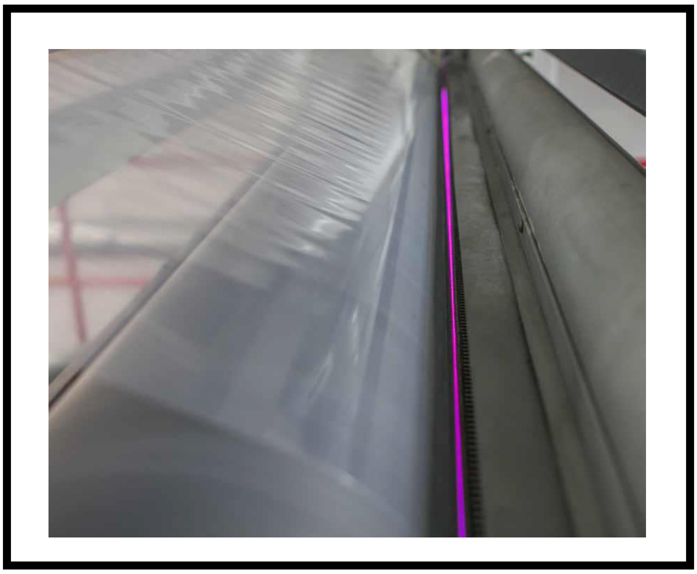


Fig-1.10: Corona Treatment being done of a moving plastic web

Following this, the gas becomes completely packed with charged species like- electrons, positive ions, and excited molecules, furthermore, heat and light energies are also produced, this assembly is generally referred to as “corona”. The generated excited molecules, being highly unstable, decompose into ions, radicals, and photons spontaneously. The theory governing the operation of corona discharge concerns with the incorporation of polar functional groups into the polymer surfaces, thereby leading to an increased surface energy ultimately resulting in a better adhesion. For instance, in the corona process involving the use of oxygen, a mixture containing activated oxygen species is used between the electrodes. The process is associated with the involvement of elemental oxygen in its free form ($O^{\cdot}$), ozone (O_3), and activated molecular oxygen (O_2*). Molecular oxygen is electrically and vibrationally excited to higher energy states to generate activated oxygen **[61].** Again, the oxygen moieties, possessing very high reactivity tend to react with polar molecules like water very rapidly and consequently, leading to the introduction of oxygen-containing functional groups into the film surface as shown in figure-1.11. On increasing the electrical power source, the production of the corona is increased and more ion formation is noticed, moreover, the particles move with an increased average kinetic energy.

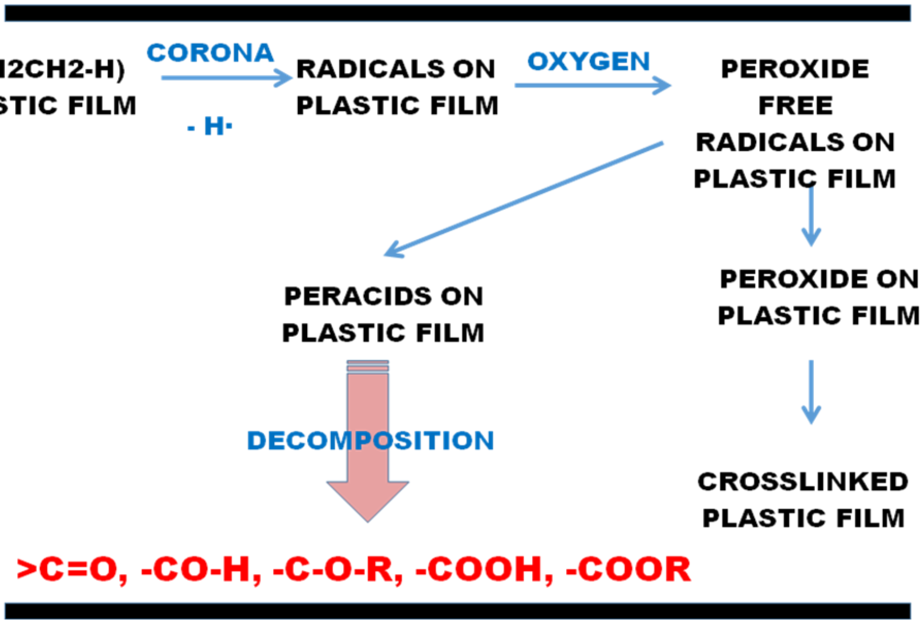


Fig-1.11: Oxygen introduction into corona discharge films

The regulation of the corona treatment level is usually done by controlling the energy of the ions that are introduced to the film. The discharge energy is expected to increase with relative humidity, as the ions transfer their energies to the aerial moisture (water molecules) **[62].**

Under conditions of elevated humidity, the corona discharge treatment results in the generation of a proportionally higher concentration of C=O functional groups. The major cause behind the surface activation was believed to be due to the electrons that are emitted by the corona-induced photo effect, leading to the changes occurring on the relevant surface both physically and chemically **[63]**. A phenomenon known as corona discharge can occur when there is a significant difference in electric potential between electrodes that are not symmetrical. This typically involves a sharp point or wire electrode and a plate or cylinder electrode. The high electric field near the sharp electrode ionizes the normally insulating air, causing ions to be attracted toward the low-field electrode.

The corona discharge can occur in different modes. Close to the threshold, both positive and negative coronas exhibit pulsating behavior, referred to as the auto-stabilization regime **[64].** As the corona voltage increases, the positive corona transforms into a continuous glow discharge, while the negative corona enters the regular Trichel pulses regime. At very high corona voltages, the negative corona also becomes a continuous glow discharge. When the voltage is further increased, streamers are formed in both positive and negative coronas until breakdown occurs. The corona discharge can be categorized as a glow discharge, where the ionization occurs primarily in the vicinity of the high-field electrode and is localized to a smaller region compared to the conduction region.

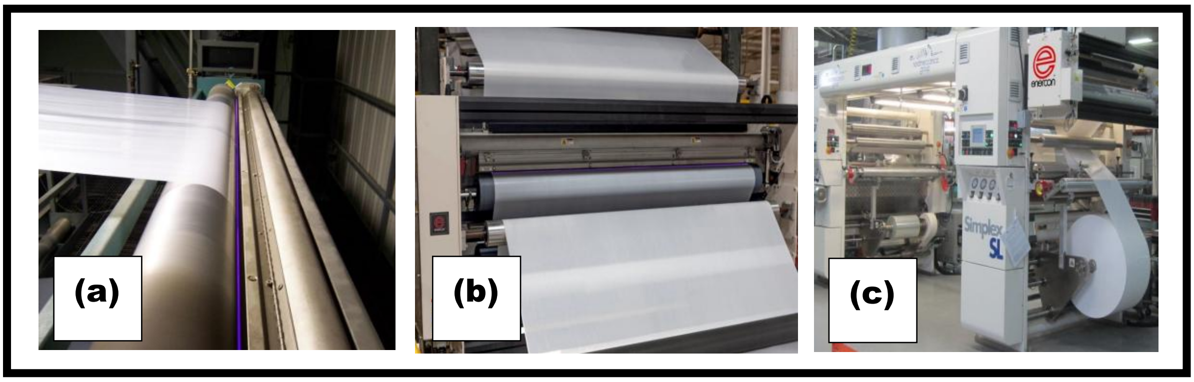


Fig-1.12: Corona Treater Unit and machine (Courtesy: A.B. Polypacks Private Limited)

This can be observed in figure-1.13 for the point-to-plane configuration. The luminescence or visible light emission is only visible in a small portion of the gap. The conduction region is characterized by the presence of charge carriers of a single polarity. These carriers have low mobility, typically on the order of cm^2/Vs. Consequently, the corona current always increases with an increase in corona voltage due to the positive differential resistance exhibited by the process. This controllability makes corona discharge a suitable method for generating thermalized ions to charge dielectric materials. It is conventionally referred to as having the same polarity as the high-field electrode. The diagram in figure-1.13 also illustrates the electric field lines, which roughly represent the path of ions. The current density distribution over the plane follows the Warburg law **[65]**, where the current density decreases with an increase in the angle ϴ (drift angle), as depicted in the figure-1.13 The glow observed near the point electrode can also produce neutral-activated species. During the process of charging polymers, these species are carried to the surface of the sample by the corona wind. The corona wind is generated by the kinetic energy acquired by gas molecules from the charged species that pass through the gap. The chemical activity of these neutral species can have a significant impact on electrochemical processes occurring on polymer surfaces. The types of ions generated in positive and negative coronas have been investigated by various researchers using mass spectrometer techniques. It has been observed that the ion species strongly depend on the gas composition. In the air, the predominant species in the positive corona are hydrated ions represented by the formula $(H_2O)_nH^+$, where “n” is an integer that increases with higher relative humidity. At low relative humidity, other ion species such as $(H_2O)NO^+$ and $(H_2O)(NO_2)^+$ become dominant. In negative coronas, the most important ions are CO_3^{2-} ions, and at 50% relative humidity, about 10% of the ions exist in the hydrated form $(H_2O)CO_3^-$. The ion species and their dependence on air humidity are significant parameters in the corona treatment of solid surfaces. In practical applications of corona discharges, where electrode spacings are typically in the order of centimeters and DC corona voltages are in the kilovolt range, the negative corona operates in the Trichel pulse regime, while the positive corona is in the continuous glow regime. Although corona discharge can cause undesired effects such as corona losses and radio interference, it has found numerous industrial applications in electrostatic precipitators, electro-photography, treatment of plastic surfaces, electrostatic printing, fabrication of electrets, and radiation detectors and dosimeters. Due to its wide range of applications, corona discharge has been extensively studied, and the current understanding of the physical processes involved in the discharge is summarized in several comprehensive review papers and books. In the charging process of solid materials using corona discharge, it is important to consider the specific properties required for various applications. As such, in electro-photography, charges deposited on the photoconductive surface need to be removed by exposure to light. In electrets, long-term charge stability is desired, as it determines the lifespan of the devices. Thus, the focus is on charge storage and transport within these solid materials. Surface potential measurements under open circuit conditions, represented by V(t), are commonly used to investigate these topics. The surface potential is determined assuming that the electric field, E(z,t), exists only within the dielectric material. This allows the calculation of the surface potential based on the integral of the electric field within the dielectric. In the past, polymer sample surfaces were directly exposed to corona point or wire discharges. While this method could achieve high surface charges, controlling the final sample voltage and achieving uniform surface charge distribution were challenging. The introduction of the corona triode was a significant improvement. It consists of a corona tip, a metallic grid, and a sample holder.

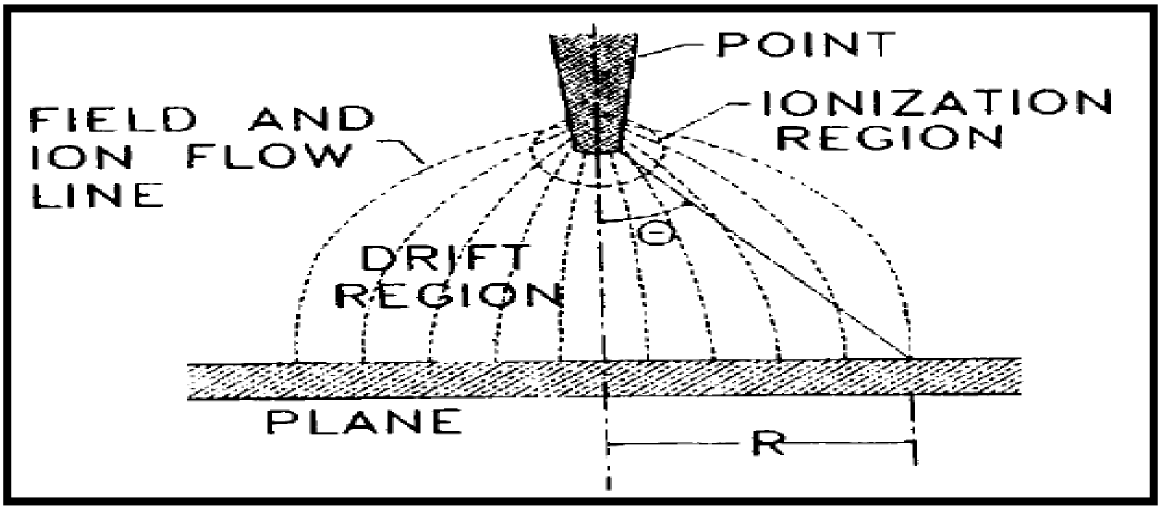


Fig-1.13: Effect of Corona discharge on a plane. [65]

It is possible to select the desired charging potential for the sample and achieve a uniform charge distribution during the charging process with a corona triode. However, typical corona triodes do not allow real-time monitoring of the sample's surface potential during charging. Surface charge decay measurements are performed after the charging process to obtain information about charge storage and transport. Various techniques such as electrostatic voltmeters, thermally stimulated current (TSC), thermally stimulated depolarization (TSD), heat pulse, laser-induced pressure pulse (LIPP), piezoelectric pressure step (PPS), and laser intensity modulated method (LIMM) can be used for these measurements. TSC and TSD techniques are commonly employed to study the charge stability of electrets. In electro-photography, the charging process of photoconductive films is relatively straightforward, but the mechanisms involved in surface charge storage and dissipation can be complex. Parameters such as the maximum surface charge density in the dark, charge decay in the dark and under light excitation, and residual potential after light exposure are crucial for evaluating photosensitive materials. Additionally, factors like charge carrier mobility, photo-injection efficiency, and breakdown effects play important roles. Theoretical models used to describe these phenomena in electro-photography are also applicable to charge storage and transport in organic crystals, amorphous materials, and polymers. Overall, understanding the corona charging process and its effects on solid materials requires considering the specific properties needed for particular applications and employing appropriate measurement techniques to study charge storage, transport, and stability. Several studies have focused on the charge decay behavior of polyethylene (PE) due to the phenomenon known as the crossover effect. The crossover effect refers to the observation that the surface potentials of samples initially charged to higher potentials decay faster and reach lower final potentials. Initially, this effect was attributed to the field dependence of carrier mobility and trapping time. However, recent research suggests that the partial charge injection resulting from large charge deposition on the polymer surface is a more probable explanation. Other factors, such as the corona treatment of the polymer surface, may also contribute to the crossover effect. Polymers, including Teflon FEP and PTFE, possess traps for electric charges that can arise from defects in the polymer structure or boundaries between crystalline and amorphous regions. The transport dynamics of extrinsic charges in polymeric dielectrics, where intrinsic carriers can be neglected, are mainly governed by the transport of free charges and charge trapping. Parameters such as trap density, trap depth in energy, trapping and de-trapping times, and charge carrier mobility are relevant in characterizing charge transport in polymers. Studies have provided insights into trap distributions in Teflon, both spatially across the sample thickness and in energy levels. Corona charging can induce phase transitions in PVDF (polyvinylidene fluoride) and cause morphological changes in the polymer surface and its trapping capability. Corona treatment has been employed to enhance adhesion to electrodes and improve the wettability of polymers such as PE, PET, and PP. Notably, corona treatment effects on trapping capability are more pronounced with high charging currents and shorter point-to-sample distances. Recent research has confirmed that ions of opposite polarity can indeed reach the sample surface during corona discharge, as shown by Chinaglia et al **[66]**. Negative corona currents can even become positive under certain conditions in a corona triode setup with a positively biased grid at a short point-to-grid distance. The occurrence of charge injection in polyethylene has also been questioned based on studies in LDPE by Das-Gupta [**67-69].**

Application of Corona Treatment

Corona treatment is widely used in the surface treatment of plastic film rolls or webs. The treatment of Corona electrical discharge over a polymer substrate prior to printing also referred to as "pre-treatment" enhances the adherence property of the printing ink on the otherwise inert polymer substrate by increasing the wettability of the substrate. In other words, the Corona treatment increases the surface energy of the otherwise inert plastic films. Thus, for inherently inert surfaces, it is quite imperative for them to be subjected to surface modifications in order to widen their industrial and commercial applications. Over the years, advancements have been made in corona processing equipment and configuration. Different types of rolls are available, including bare rolls, covered rolls with dielectric materials, and universal rolls with proprietary ceramic coatings. The choice of roll covering depends on various properties, such as dielectric strength, heat resistance, and cost.

The effectiveness of corona surface treatment depends on factors such as watt density, line speed, and the substrate surface. The watt density is influenced by power and station size, with higher power and smaller station size resulting in higher watt density. The response of a material to corona treatment varies based on its type and surface quality. For example, certain polyesters show a significant increase in surface tension at low watt densities, while polyethylene and polypropylene require moderate and high watt densities, respectively, for significant surface tension increase. While corona treatment is successful in enhancing wettability and adhesion of plastics, it can also have some disadvantages and negative effects. These include an increase in surface roughness, formation of pinholes, and surface changes that may become unstable over time. The filamentary discharges in the corona process can create high-energy point locations in the air gap, leading to surface damage and heterogeneous treatment effects. Additionally, non-uniform ionized air can cause significant surface morphology changes and damage to surface macromolecules. The reactive gas, plasma, and corona discharge processes offer environmentally benign, versatile, and reproducible methods of surface modification. Furthermore, reactive gas processes-including plasma and corona, are suitable for being applied to very thin surface layers or deposits, single/multilayered coatings (primarily polymer-based), without causing any alteration to the bulk properties of materials.

Physical, Chemical and Morphological Changes due to Corona Treatment

Overall, corona treatment is an effective surface modification technique for plastics, which warrants careful consideration of its potential drawbacks and suitability for specific applications and materials. The corona treatment process being an atmospheric pressure method for modifying the surfaces of plastics, involves the application of an air electric discharge to enhance the surface properties of polymer films. In an extrusion line for films, the corona process is typically employed in-line before printing.

When voltage is applied to the electrodes, energy is transmitted to the air, leading to the formation of small filamentary discharges comprising ionized air. The energetic species created in these discharges break surface covalent bonds, resulting in the formation of radicals, cross-linking of surface macromolecules, and oxidation of surface functional groups. The oxidation process generates new surface polar groups, such as hydroxyl, carbonyl, amide, and carboxylic acid, which increase the surface energy and wettability of the plastic film.

Corona treatment has the ability to create polar chemical functional groups on the surface of polymers, leading to improved surface adhesion and wettability. Additionally, it has been observed that corona treatment can cause changes in the morphology of polymer films, which can in turn affect their adhesion properties. The impact on adhesion can vary, with some cases showing increased adhesion due to larger bonding areas, while others may experience decreased adhesion due to the presence of voids. When corona discharge treatment is conducted in the presence of air, significant morphological and chemical modifications occur in the surface of the polymer. These modifications can alter the external appearance of the material and result in the generation of functional groups. The extent and nature of these changes depend on the specific treatment techniques and the polymers involved.

Corona discharge treatment induces chemical changes on the surface of polymers, leading to an increase in surface energy and the introduction of polar groups. This improvement in surface properties enhances adhesion and wetting characteristics. The primary chemical mechanism involved in corona discharge treatment is oxidation. Additionally, the treatment promotes the crosslinking of surface molecules, which restricts their mobility and results in an increase in molecular weight.

Chemical changes occur in polyolefins through air oxidation and photo-oxidation processes. These changes were first detected in the 1950s using transmission infrared spectroscopy. In thermal oxidation, keto groups are mainly formed, along with some aldehyde and acid groups. Similar quantities of aldehyde, acid, and keto groups result from photo-oxidized polyethylene. Changes in unsaturation levels indicate the formation of unstable hydroperoxide groups. Various polar functional groups, including hydroperoxide, ketonic, alkoxy, and carbonyl groups, have been identified. The oxidation of polymers by atomic oxygen rapidly occurs at the surface. Thermal oxidation begins with the slow formation of hydrocarbon radicals, which react with oxygen atoms or molecular oxygen along with alkoxy or hydroxy radicals. Comparative studies have been conducted on corona treatment effects in various atmospheres, including air, oxygen, nitrogen, helium, and argon. It has been found that corona treatment in inert gases can still incorporate oxygen into the film surface, resulting in the creation of ketonic functional groups. These groups can participate in hydrogen bonding with carbonyl groups in ink or coating binders, enhancing adhesion.

Oxidation also plays a significant role in the auto-adhesion of polymer films. Enhanced adhesion between polymer layers after corona treatment is attributed to hydrogen bonding between hydroxyl groups of enol and other oxygen-containing functional groups formed on the polymer surface. Corona discharge in a hydrogen atmosphere prevents the formation of oxygen functionalities and does not promote auto-adhesion. Corona discharge treatment increases the molecular weight of polymeric materials. The introduction of free radicals during corona discharge leads to higher molecular weight, resulting in improved strength, higher melting point, and greater integrity of the treated surface. Surface oils and waxes are incorporated into the stronger high molecular weight boundary layer, increasing its thickness. Studies have also shown that corona discharge treatment induces surface crosslinking in polyethylene, as observed in heat-sealing studies. The presence of peroxyradicals can cause either chain scission and reduced molecular weight or chain addition and increased molecular weight, with the prevalence of the reaction influenced by corona treatment power levels. Corona treatment not only introduces polar functional groups on the surface of polyolefin films but also alters their surface morphology. The polar component of surface energy plays a significant role in understanding the adhesive behavior of the treated films. Changes in surface morphology can impact the level of adhesion achieved. During corona treatment, the film surface undergoes changes in surface morphology. High-energy particles bombard the film, creating small micropits or tiny holes. These micropits can have both positive and negative effects on adhesion. The outcome depends on factors such as surface energies, the viscosity of the wetting liquid, and the size and shape of the irregularities. Corona treatment in the presence of air or oxygen has been found to roughen the surface of polyolefin films. Surface roughening is more significant when pure oxygen or carbon dioxide is used instead of air. In contrast, corona discharge in gases lacking oxygen, such as hydrogen, helium, argon, or nitrogen, does not visibly alter the surface. This suggests that oxidation is a necessary component for the surface roughening effect to occur. Over-treatment can lead to the formation of bumps on the polyolefin surface, which negatively affects adhesion and wettability. In extreme cases, excessive heat generated during the process can cause the treated samples to burn. The surface morphology changes with both the duration and temperature of the treatment. Longer treatment times and higher temperatures generally result in larger bump sizes. For example, a 1-minute treatment at 50°C creates bumps around 1 µm in diameter, while a 15-minute treatment at 75°C produces 10 µm bumps. Polyolefin films treated for extended periods at elevated temperatures exhibit reduced bond strength and have a looser surface compared to films treated for shorter durations. This suggests that the degradation products generated during over-treatment may contribute to weaker self-adhesion.

In a nutshell, corona treatment induces changes in surface morphology, resulting in roughening of the surface by way of forming of micropits, and at the same time, excessive treatment can lead to undesirable surface effects and compromised adhesive properties. The severity of these changes depends on the treatment conditions. Hence controlled treatment is the call of the day for achieving the desired degree of adhesion.

1.8. Scope

Polyethylene (PE) plays a key role in modern-day Packaging mainly because of its versatile properties, easy processing, and lower cost input. On the flip side, PE consists of non-polar, saturated, high molecular weight not covalently linked hydrocarbons making it almost inert. In its common form, it can neither be printed nor laminated with other suitable substrates because of very little affinity. The corona treatment on PE has been found effective in overcoming this surface property to a large extent. There is a dearth of scientific studies about the applicability of corona treatment in modifying the surface properties of PE. Hence the doses of corona treatment and wattage, in order to achieve the desired surface energy or treatment are assumed only and not designed. The industry is in dire need of a standardized procedure to enumerate the level of surface treatment/energy and its economic application which warrants a detailed scientific study of physical and chemical influences of corona treatment. TiO_2-embedded opaque LD/LLDPE film is known to show increased opacity to inhibit the transmission of sunlight and protect the contents from the deleterious effect of light, higher barrier properties, and penetration of moisture through the film than a transparent film of identical thickness resulting in enhancement of the shelf life of the products. However, there is no published literature on this subject. In order to reciprocate the call of the industry, the instant study is envisaged to study both the above aspects along with the influence of TiO_2 on the level of charge development at the different applied voltages employed for corona treatment.

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Chapter 2:

LITERATURE REVIEW

2. LITERATURE REVIEW

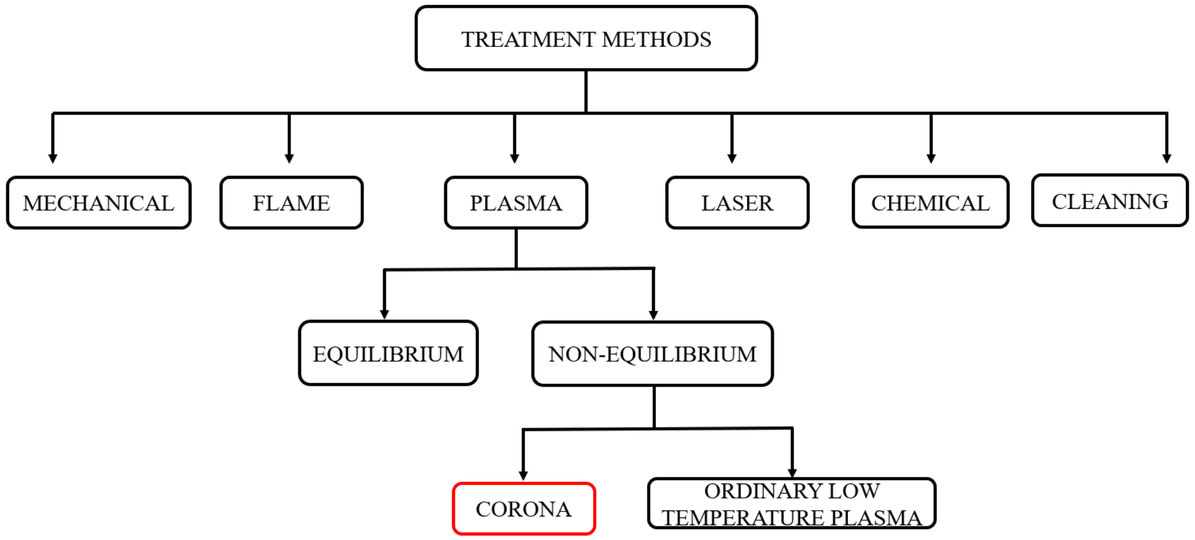
This chapter chiefly concerns a comprehensive documentation on the work done so far involving necessity of physico-chemical treatment on the surfaces of plastics, a concise discussion on the different methods of such treatment, relative advantages and disadvantages of these methods. The reasons as to why the particular method of “Corona Treatment” has been selected as the topic of present dissertation, the physical and chemical attributes of corona treatment on the plastic film surfaces and lastly a brief review of the causes pertaining to the widespread applicability of corona treatment in spite of the most modern methods as in existence.

Plastics, the polyolefinic film surfaces in particular have inherently low surface energies due to their hydrocarbonaceous nature leading to non-polar and inert surfaces **[1].** Loosely bonded materials may originate from the plastic part itself and from additives incorporated during its fabrication such as pigments, process aids and mould release agents. These loose contaminants may impair the surface adhesion characteristics. Thus, the inert and non-reactive surfaces of such films do not allow any further processing to be carried out on its surfaces. The poor spreadability and wettability prevent any coating medium to get proper anchorage on it. Owing to high chemical resistance, polyolefins are impossible to join by solvent cementing. Normal solvents (organic) can neither penetrate the non-porous surface nor they can spread and wet the film surface properly. This is why the conventional solvent laden printing inks and adhesives can be used neither for printing nor for laminating with other substrates. This necessitates modification or treatment of its surfaces that can activate the surface molecules, enhance its surface energy to the level that would allow wetting, spreading and adhesion.

2.1. Changes on Plastic Surfaces due to Treatment

Some changes occur at plastic surface by the action of different treatment methods. Common methods of treatment are corona, flame, plasma and chemical etching, all of which help to increase the surface energy of plastics. The polar component of surface energy increases by 15-20 dynes/cm which confers proper adhesive bonding in polymers such as polyolefins, PPS and polyamides [**2**].

2.2. Treatment Methods



2.2.1. Mechanical Treatment

Similar to the surface treatment processes like sanding and roughening carried out on metals, plastics may also be subjected to such operations aiming at similar outcomes. The low MW polymer chains along with some unreacted monomers or some other small molecules agents are essentially removed from the surfaces, thereby increasing contact surface area. However, such operations are not feasibly carried out while printing, coating or lamination of thin plastic films applicable for flexible packaging. Thus, process like hand-sanding or sand-blasting have limited applications when employed for plastics.

2.2.2. Flame Treatment

Flame treatment is one of the first physical types of surface modification methods applied to plastics. It is associated with the incorporation of oxygen-bearing polar functional groups into the surfaces of non-polar (such as PE, PP etc) and somewhat less polar (for instance, PET and polyacetals) polymers, which are responsible to primarily enhance wettability, adhesion and printability of such surfaces. Flame treatment processes and the related set-up are relatively easy to fabricate and operate. The dimension and shape of the material govern the number of burners to be used. In order to flame treat plastic blow-moulded bottles with uniform modification throughout, three burners are normally required. The surface modification of polymers is generally accomplished by means of surface oxidation, for which the burners are injected with a controlled ratio of air and gas mixture.

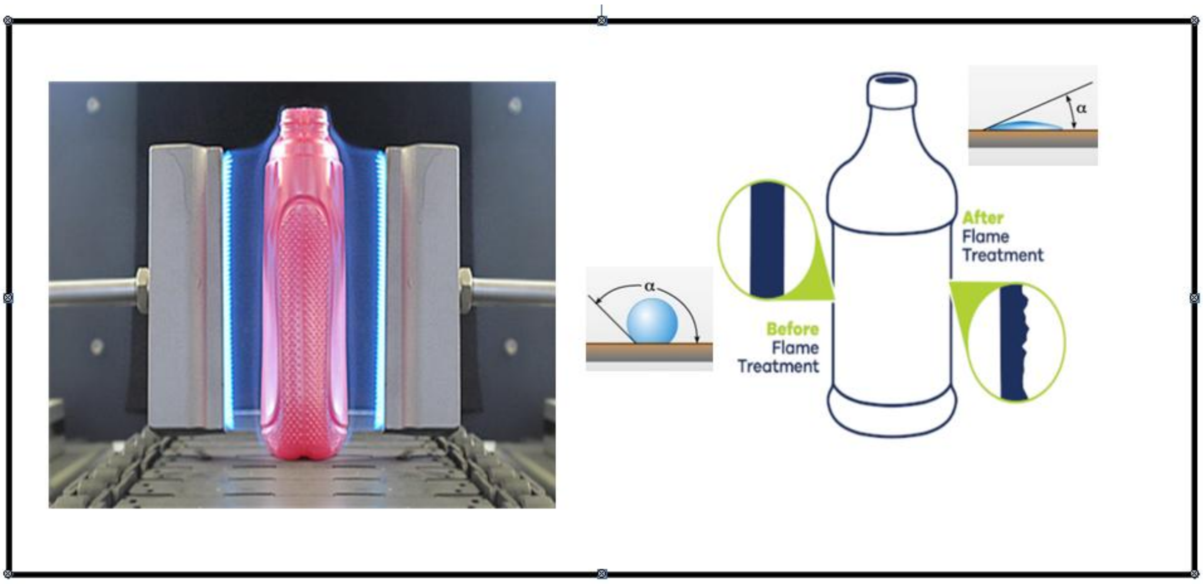


Fig-2.1: Contact angle changes upon surface treatment

Spectroscopic studies like- XPS and SIMS that concluded the fact that oxygen-bearing groups can be incorporated on surfaces of PE and PP following flame treatment **[3-5].**As per reports, the flame oxidation process is not likely to be interfered by the presence of antioxidants. This is corroborated by the fact that the flame oxidations get initiated by the abundantly present free radicals in the flame and rather not due to the slow generation of free radicals within the polymeric chains **[6]**. The flame treatment method being substantially cheap and simple in terms of its application, makes it widely applicable to the packaging industries including the surface treatment of blow-moulded bottles and thick polymers **[7].**

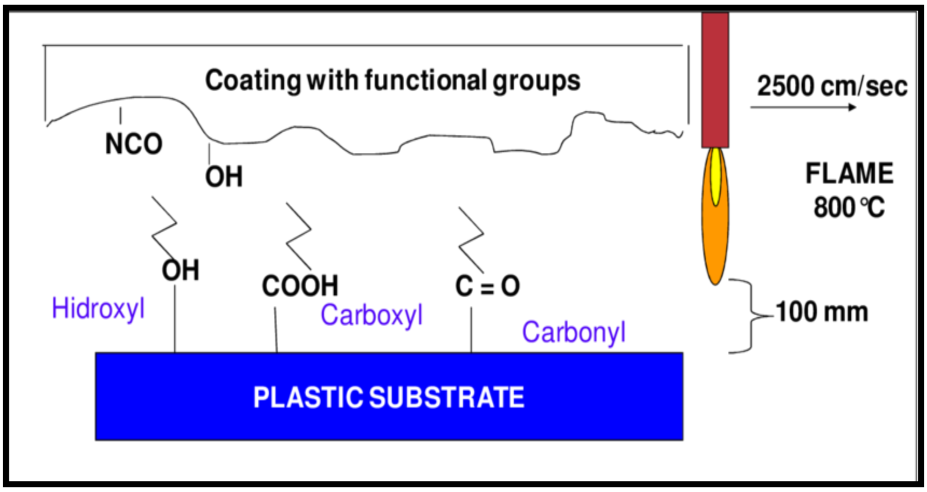


Fig-2.2: Functional groups developed upon surface treatment

In order to obtain an optimum level of surface modification, some operational measures that need to be adopted for flame treatment method includes-the close monitoring of the temperature, contact time, composition, flow rate of the flame as well as the gap between the flame and the polymer surface**[8].** For instance, normal contact times are kept below 1 second as on prolonged exposure to flame may lead to the burning of the plastic. Measured steps must also be taken in order to prevent surface contamination following flame treatment due to the chemical action of various residues or partially burnt products subsequently produced due to the treatment process. This ensures that there is no consequent effect involving formation of a weak boundary layer at the interfacial surface of the polymer leading to the loss in their adhesion characteristics to any extent.

2.2.3. Laser Treatment

Laser-based modification processes of polymer surfaces have become immensely popular recently with the onset of developments in laser systems in terms of their industrial applicability and the involved economics. Although, in relation to other existing physical treatment methods of surface modification, the laser method involves a higher capital cost, but is associated with high precisional supremacy. Hence this type of surface treatment finds applications primarily in the fields of electronic, optoelectronics, material processing, aerospace and automotive sectors where high level of precision is desirable.

The fundamental behind the working of a laser involves atomic excitation from its ground state to an excited state possessing a higher energy by the application of a high voltage. In due course of excitation, atoms loose electrons to become positively ionized and consequently migrate towards the cathode, whilst the removed electrons move towards the anode. The series of such events ultimately lead to the emission of radiation possessing a characteristic energy, wavelength and frequency. The emission ceases on removal of voltage, while the atom reverts to its ground state. The inherent characteristics that make the laser-based technique highly desirable for surface modification include high tunability, monochromatic behaviour, broad range of powers and pulse durations (which make them highly applicable for surface treatment of various materials with minimal heat damage). The different types of lasers employed for surface modifications include –

i) CO_2 lasers,
ii) Nd:YAG lasers,
iii) excimer lasers **[9]** having various characteristics.

The CO_2 and Nd:YAG lasers are operative in the IR domains of the electromagnetic spectrum and thus are applicable to processing of metals such as cutting and drilling, since such materials are undergoing dissociation to produce molecules upon thermal excitation. Hence, these types of lasers are not suitable for the polymeric surface modification since they generally result in various undesirable outcomes including combustion, melting, charring etc. Contrarily, the other type, excimer lasers, are capable of operating in UV region, allowing polymers to strongly absorb the UV radiations. Photochemical processes are subsequently induced by the absorbed energy thereby altering surface characteristics without causing any adverse over-heating related effect to the polymeric material. Adhesion properties play a very vital role in the packaging sector, especially in food packaging. Good adhesion attributes are highly necessary to ensure minimal leakage, low risk of microbial contamination and many more. Moreover, adhesion properties are ultimately associated with the food safety, especially for flexible and semi-rigid packaging during the transportation and storage of the product. Poor adhesion between the polymer-adhesive makes packages vulnerable to failure during their transit and handling. Furthermore, any interaction between the packaged item(s) and the used adherents may also lead to an integrity loss to the package or may ultimately affect the barrier and mechanical properties adversely, thereby lowering the quality and shelf life. Hence, the adhesion characteristics between polymers-adhesives require improvement in order to achieve an acceptable seal strength ensuring the product integrity. In this regard, the mainly challenge is posed by the very low surface energy of the polymers. Breuer and his co-workers concluded that the strength of adhesion of epoxy-based adhesives over PP films could be substantially improved by adopting the surface treatment method involving photochemical reactions **[10].**

The report conferred the formation of oxygen bearing functional groups viz. –OH and –C=O groups which happened play the primary role behind enhanced adhesion achieved upon projection of characteristic UV excimer laser on PP surfaces under specific surrounding environments. This report was followed by another finding by a group which established a correlation of adhesion strength of PP films with various attributes of the UV excimer laser which includes wavelength of radiation, its pulse number and energy density **[11]**.

Surface characteristics of PET films were studied by Chtaib et al. by using UV excimer laser source operated at 193nm wavelength under three different atmospheres of air, O_2 or N_2 resulting in different surface behaviours varying with the applied energy densities **[12]**.

According to the findings, drastic deoxidation of the PET surface was found to occur at low domains of energy densities (<20 mJ/cm^2), owing to the elimination of gaseous products like CO and CO_2. The presence of oxygen bearing functional groups like –C–O and –C=O was successfully detected on the surface PET samples by means of XPS studies. The incorporation of such polar groups significantly enhances the surface adhesion properties of PET, a vital polymer widely used in food and other packaging industries. Some more studies have also reported enhanced adhesion and wettability of plastics with other polymers or metals by means of UV excimer **[13-14]**.

High adhesion in laminated materials is vital to ensure the integrity of the package and to obtain stable food products during their storage. This, in particular, is highly necessitated in aseptic packaging of commodities like milk and fruit juices. For fabrication of laminates, inferior adhesion characteristics of plastics with other polymers, metal foils or paper may lead to delamination thereby allowing the food items to come in contact with the package which may result in future failure of the package.

In another study, Frerichs et al. were successful to modify the surface properties of various polymers used in food packaging (PP, PS, and PC) by means of a UV radiations operating in air **[15]**. Such polymers have shown improvement in their adhesion behaviour with a variety of metals including aluminium, copper, nickel and titanium even before the metal-coating process. Moreover, laser-based surface modification techniques are known to produce highly desirable aluminium films devoid of any surface cracks appropriate for food packaging. Owing to superior mechanical and barrier properties, these films are less susceptible to package leakages, permeation of gases and water vapour across the packaging and risks of microbial contamination. Such metallised packaging films are suitable for carbonated beverages, food items which are vulnerable to exposure to light, oxygen and moisture. Additionally, such films could also find applications in aseptic packaging **[16].**

Another report claims for the successful deposition of silicon dioxide on polymeric surfaces by means of UV excimer laser-induced processing **[17].** Owing to the food safety characteristics of silicon dioxide, the prospect of silicon dioxide deposited polymeric films is expected to be very high for food packaging applications. In Japan, this technique has been employed over the interior layer of rigid packaging using a very fine glass coating in order to restrict flavour sorption as well as to prevent various other interactions that exist between food items and the packaging materials. Such plastic films coated with glass layering exhibit various advantageous features including microwavability, low transmission rates of water vapor and oxygen **[18].** The UV excimer laser technology has been phenomenal in imparting antimicrobial properties to packaging films which are highly desirable for food products. The introduction of amine groups on polymeric surfaces through modification techniques have been proved to play the major role behind their antimicrobial activities by virtue of which such surfaces are capable of killing microorganisms that come in contact with the surfaces **[19].**

In nylon films, the conversion of amide functional groups into amines at the surface was accomplished by UV excimer laser treatment method resulting in antimicrobial activities **[20]**. The importance of antimicrobial properties for food packaging is immense as it ensures minimum microbial contamination with the food items during transit and storage. Hence, increasing their shelf life and complying with food safety protocols. The demand for antimicrobial packaging is much higher for ready-to-eat foods as these products are readily consumable, that too, in the raw or semi-cooked form. Some antimicrobial films contain antioxidants, impart specific flavours to the food items and release controlled amount CO_2 as well. Laser-based surface modification techniques could also be adopted to impart enhanced and controlled release characteristics to different films used for various packaging applications **[16]**.

2.2.4. Chemical Treatment

Although physical methods of surface treatment serve the purpose to certain level, there are some areas where such conventional methods become inadequate to cater industrial requirements. Chemical surface treatment techniques, in most cases are associated with wet procedures involving dipping, coating or spraying of the polymer in/with a chemical so as to obtain enhanced surface properties and also to facilitate removal of dirt and microbes from the surface. This is particularly important in case of biomedical applications which demand a sterile environment (Figure-2.3).

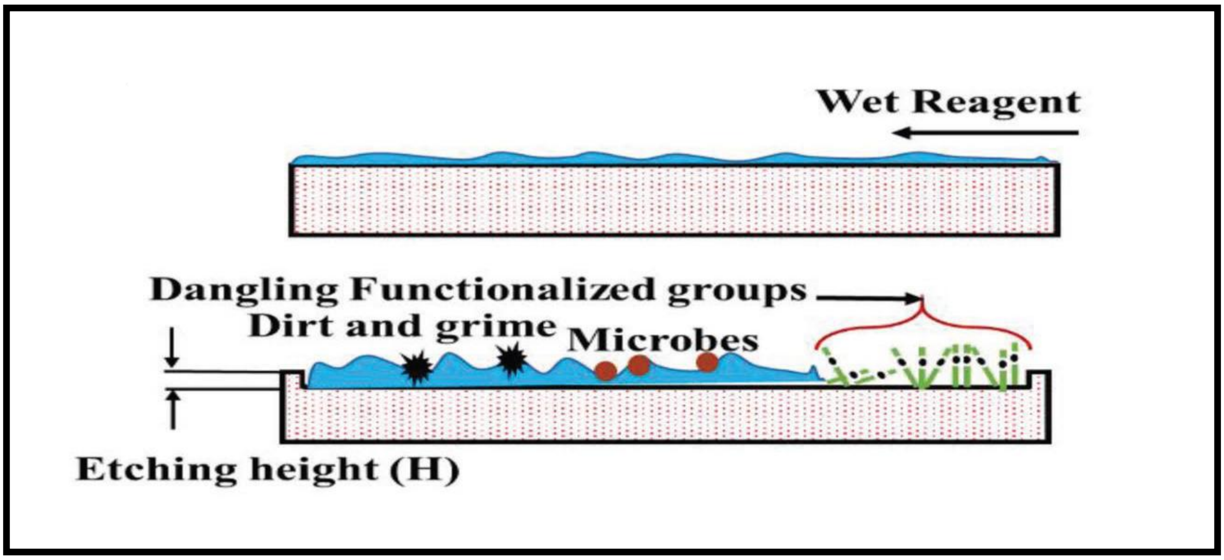


Fig-2.3: Action of chemicals on substrate surface

Surface energy of substrates could be increased by employing wet chemical etching method by inserting oxygen-borne functional groups on the surface. The method involves solvent penetration into the matrix of the substrate, usually a polymer, making the process highly effective and cost-effective. The chemical method has got a wide range of applicability. The action of oxidising agents like $KMnO_4$ or $K_2Cr_2O_7$ on polymeric surfaces has been discussed by a work by Siau and co-workers. The chemical treatment was found to generate surface roughness on the applied substrate by the layers located at the top section **[21].**

Another study dealt with the surface treatment of nylon by using a solution containing a mixture of iodine and potassium iodide. It was reported that the surface adhesion enhancement was directly proportional to the extent of crystallinity and molecular weight of the polymer **[22].** Improved adhesion properties were also observed by chemical treatment of polypropylene by using strong base like sodium hydroxide which resulted in better cell attachment despite sustaining the mechanical properties of the polymer [**23**].

Whilst, an enhancement in adhesion characteristics was reported by means of acid treatment on epoxies [**24**].Chemical treatment of PET films could be achieved by using acetonitrile, permanganate and sulfuric acid in tandem. This resulted in the generation of fresh carboxylic acid functional groups on the surface **[25].** In the field of electronics, adhesion between polymer surface and metal has a very crucial role to play. Wet chemical treatment techniques facilitate such a reinforcing adhesive strength to polymers **[26].**

According to Schaubroeck and co-workers, the adhesion properties of resins having dielectric nature with metal deposition get enhanced due to the incorporation of amine functional groups **[27].** Surface modification of polymer through functional groups exhibiting strong electron affinity, for instance fluorine achieved by means of solution reactions, chemical vapor techniques increase their tendency to withdraw electrons **[28].**

Surface modification also affects the electrical properties of a substrate. A report claims that by means of selective functionalization of polymers their triboelectric polarities could be increased by the action of charged reactive species that remain covalently bonded to the surface of the surface **[29].**

Post-treatment, the polymers showed a greater open-circuit voltage along with better performance stability for prolonged time. Actually, the conventional wet chemical techniques are considered to be more feasible and economical, but focus must be attempts aiming at lesser waste generation following processing. There has been a demand for the development of alternative methods featuring higher sophistication, contact-less mode of working and higher efficiency. On one side, for adopting wet chemical treatment methods, a wide range of reagents are available to carry out treatments to polymers selectively, that too at a large scale with minimum cost, but on the hind side there involves a requirement of a meticulous approach since the reaction rate depends on the reagent strength, composition of material and treatment duration. Furthermore, accessory processes including cleaning, rinsing, washing, drying etc need to be carried out prior to further polymer processing. Such operations in most cases, add to the generation of hazardous wastes generated also increase the involved cost. Hence wet chemical routes of surface modification are recommended mainly for non-invasive type of application, causing very less amount of side effects for example proactive etching etc. Moreover, it is not associated with major end-application concerns related to bulk changes in their morphological structures such as crystalline phases.

2.2.5. Cleaning Methods

Thorough cleaning of substrate is necessary prior to application of bonding adhesive and other types of coatings. Adherends with uncleaned surfaces would not be receptive to any foreign applicants and thus, would lack proper adhesion characteristics. In many cases, the adherend surface preparation necessitates further post cleaning operations. Cleaning, being a physical method of surface preparation involves the removal of various common contaminants such as oil, grease, dust particles, finger prints etc. In order to make the surface adhesion receptive to an optimum level, some other physical and chemical treatments are required to be carried out. Such requirement necessities are best exemplified for fluorinated polymers such as PTFE. Various metal surfaces also require such treatment methods in order to facilitate adhesion on their surfaces. “Cleaning” is a broad term which refers to the removal of surface contaminants including dirt, oils, grease etc, while it also covers surface treatments via chemical routes for enhancing adhesive bonding [**30**].

Cleaning could be categories into three types based on its sequential occurrence:

i) Solvent cleaning

ii) Intermediate cleaning

iii) Chemical treatment

Either one, two or all the three above mentioned operations is/are required for the preparation of any surface. In certain case, surface priming may also be executed in order to achieve better and more durable bond strength even under drastic ambient.

2.2.5.1. Solvent Cleaning Method

This process is associated with the elimination of soil particles from the surface of a substrate with the help of an organic solvent, devoid of any physical or chemical alteration to the material (substrate). There are various techniques by means of which solvent cleaning can be accomplished namely spraying, vapour degreasing, immersion and ultrasonic scrubbing. In a series of cleaning and chemical modification technologies, solvent cleaning can be a preliminary step **[30].**

Fig-2.4: Solvent cleaning technique being applied in the industry

The basic procedures for solvent cleaning may further be classified as the following:

- Solvent wipe, immersion, or spray
- Vapor degreasing
- Ultrasonic vapor degreasing
- Ultrasonic cleaning with liquid rinse

2.2.5.1.1. Vapor Degreasing

This procedure is associated with the removal of oils, greases, soluble soil particles, waxes and particular matter including both metallic and non-metallic. The main step of this technique deals with the scrubbing of the surface with hot solvent vapours, which condense over the substrate surface at an acceptable rate causing the liquid to flow. This flowing liquid washes away soil particles by dissolving them, the flow driven by the action of gravity. This technique necessitates the requirement of appropriate solvent as well as degreasing equipment.

The solvents suitable for degreasing must possess certain attributes including the following-

i. Non-flammability, non-explosive and inert nature under application conditions
ii. Higher value of vapor density than that of air
iii. low air diffusion rate in order to reduce vapour loss
iv. Low specific heat as well as heat of vaporization to increase condensation while minimizing heat consumption

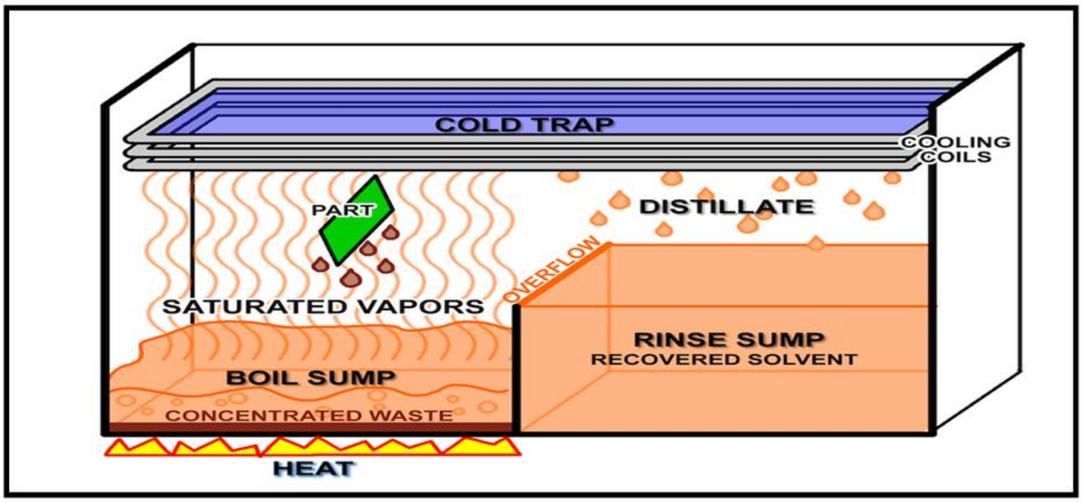


Fig-2.5: Vapour degreasing equipment

v. Optimum Boiling point in order to ensure ready distillation and simultaneously providing ease of condensation (required to recycle, reuse or regeneration of contaminated solvent, post-cleaning)

vi. Greater capability to dissolve oils, greases, and other particular matter present in soil

vii. High chemical stability

viii. Non-corrosiveness

ix. Operation safety

x. More eco-friendly in terms of air pollution

2.2.5.1.2. Ultrasonic Vapor Degreasing

This is a vapour degreasing method involving the use of an ultrasonic transducer along with a solvent cleaning rinse tank. The first step involves the cleaning the substrate either by rising with vapour or by immersing in a boiling solvent. Next, the substrate is subjected to ultrasonic scrubbing and subsequent rinsing using vapour or spray. The ultrasonication is associated with the transmission of sound waves having high frequency range through a solvent to the surface where the intended treatment is supposed to occur. This produces cavitation on the surface by means of which high energy is transmitted to the soil particles present on the surface. This facilitates ready removal of various contaminants like insoluble matter and particulates that remain strongly adsorbed onto the surfaces from every corners of the substrate. The frequency and intensity of the ultrasonic wave depends on the type of contaminant to be removed.

2.2.5.1.3. Ultrasonic Cleaning with Liquid Rinse

Cleaning of surfaces involving ultrasonic waves is a common procedure to bring about cleaning of high quality. A small modification to the ultrasonic vapour process is the one under discussion, which involves the use of liquid solvent for rising following an ultrasonic perturbation. This process has no limitations for the usage of type of solvent. Most widespread applications include the use of various aqueous solutions like those of surfactants, detergents as well as acidic or alkaline cleaners. Some of the necessary criteria for this technique includes the fact that the solvent must not react chemically with the substrate, it must not form foam in large amount and lastly the solvent must be able to cavitate the surface adequately in order to facilitate effective cleaning. Compared to the other techniques like vapour rinsing, immersion or spraying, solvent wiping, this method is less efficient, nevertheless, it's quite suited for several surface preparation and pre-treatment applications. Generally, a combination of the methods is recommended.

2.2.5.1.4. Solvent Wipe, Immersion or Spray

The most versatile and portable techniques of surface preparation is solvent wiping, though its controllability is very poor, by virtue of which it poses the risk of incomplete removal of surface contaminants. The requirement for applying this method involves the proper cleanliness of the wiping materials- cotton, rags, cellulose tissues etc. The use of solvent in this technique is only for one time, being applied on the wiping material. This is a cyclic process which requires discarding of the wiping material after a single use. In spite of the efficacy of immersion and soaking processes in the solvent, sometimes scrubbing becomes necessary particularly when intended to remove heavier soil particles. Apart from ultrasonic scrubbing, other methods associated with scrubbing are solvent agitation, tumbling, brushing and wiping. Following the operations of scrubbing and soaking, rinsing the substrate surface is mandatory, upon which the cleaning efficiency is dependent. The solvent may also be applied by spraying it on the surface of the substrate thereby cleaning it. This method has been found to be efficient owing to the scrubbing effect caused due to the impact of very fast-moving solvent molecules on the surface to be treated. The solvent impingement results in washing away of the loose soil particles present over the surface. Unlike the immersion technique, this method of surface cleaning is devoid of any risk of surface contamination as the solvent molecules are simply poured over it by spraying.

2.2.5.1.5. Precautionary Measures for Solvent-Based Cleaning Methods

Some primary safety protocols must be adopted while handling solvents applicable to cleaning operations. These are related to certain integral attributes associated with different solvents such as-

- flammability
- toxicity
- compatibility
- risk of hazard

as well as the equipment involved.

2.2.5.2. Intermediate Cleaning Method

This technique as well, relates to the removal of soil particles from a surface of a substrate through mechanical, physical or chemical routes without affecting the chemical composition of the material. During the process, a little amount of the substrate material may be scraped off. The different types of intermediate cleaning technique include- Grit blasting, Sanding, Wire brushing, Abrasion scrubbing, alkaline cleaning and cleaning by detergents. Intermediate cleaning must always be preceded by solvent cleaning methods. Some common applications of intermediate cleaning are cleaning of stainless-steel surfaces using alkaline cleaner, cleaning of epoxy laminates by means of detergent scrubbing etc. In the following sections let us discuss in brief the various types of intermediate cleaning.

2.2.5.2.1. Grit Blasting

Grit blasting method is most commonly employed to produce enhanced adhesion of coatings based on fluoro-polymer. Preheating must be carried out on surfaces of ferrous metals prior to the application of grit blasting method in order to retain the generated protective oxide. The sequencing of these two operations is not strictly maintained for other materials. The grit blasting technique has been considered to be a comparatively simple process [**31**]. Propulsion of hard grit is accomplished by using compressed air as well as using high-pressure water, at times, thereby leading to surface cleaning and/or roughening. Aluminium oxide grits are normally used on hard surfaces operating at air pressures ranging between 80 to 100 psi. An air pressure of 100 psi or higher may be employed for stainless steel. Various types of grits are available in the market. The selection of grit is based on the application, the material as well as on the involved economics. Hardness is an important property of a grit. Soft surfaces like that of plastics, demand minimal damage. Such cases may apply plastic grit, walnut shells or even sodium bicarbonate. Pan and co-workers studied the effect caused by grit blasting having various abrasive particle dimensions on laminates made from hybrid materials- Mg/CRFP. The roughness of the surface was found to increase with particle size [**32**], which in turn showed a similar effect on the peel strength of the relevant laminate. Whilst, the increment in the shear strength was found to be nominal. Another group of researchers discovered an enhancement in bonding characteristics between polyamide and AA6082 following grit blasting technique. The impingement pressure was also found to assist the bonding characteristics [**33**]. The blasting technique using sodium bicarbonate has a uniqueness which is associated to its biodegradable features. This method is used for soft, delicate and sensitive substrates. For some its common applications include removal of graffiti, to clean boat hulls and over large sized printing press rolls. They are normally used in form of water-based slurries operated at high pressures.

2.2.5.3. Chemical Cleaning Method

Cleaning techniques involving chemicals operate by chemically reacting with the surface contaminants over a substrate. There occurs a chemical modification of the surface leading to an improvement in its surface adhesion characteristics. Chemical treatment operations are always carried out subsequent to solvent cleaning; sometimes the intermediate cleaning method is also employed in between.

2.2.6. Plasma Treatment Methods

Plasma, considered to be the fourth state of matter, is also termed as glow discharge. It consists mainly of charged particles- positive and negatively charged ions, while other types of minute entities may also be present, for instance- atoms, molecules or even free radicals. Plasma discharge is generated by the action of electricity to excite a gas. The plasma state has been known to be electrically conductive and it is responsive to the influence of magnetic field as well. Thus, it is highly reactive. Plasma was first reported by Schonhorn and Hansen in the year 1966, applied over the surface of a polymer having low surface energy. Plasma treatment is mostly used to enhance surface adhesion in plastics **[34]**. It functions by making the surface of any material rougher, substantially wettable thereby making the same more adhesion conducive. The key attribute to this process is the requirement of low pressure. The plasma treatment technology is majorly associated with the exposure of a polymeric surface to a plasma of an inert gas, under low pressure conditions, which is generated by an electrode-less glow discharge. Reports confer very short treatment durations for PE surfaces, whereas for other polymers like PTFE, prolonged contact times were necessary [**35**]. The working action of plasma on polymeric surfaces involves the expulsion of atoms which results in the formation of a crosslinked top skin possessing enhanced roughness, strength and wettability **[3]**. Plasma treatments could be applied to various types of plastic parts, furthermore on the surfaces of powdery additives such as fillers, pigments etc. In spite of all the key advantages of plasma treatment methods, it finds limited applicability industrially for itself, owing to the involved expense and process constraints leading to overall inconvenience. Moreover, the execution of plasma treatment requires the presence of vacuum.

Generally, the plasma technology can be divided into two broad categories- equilibrium plasma (heat or thermal plasma) and non-equilibrium (glow-discharge or cold plasma) [**36-39**].'Cold plasma' is produced by the introduction of the selected process-gas into a vacuum chamber which is subsequently excited by an energy source having a frequency in the domain of radio waves or microwaves. This result in the dissociation of the gas molecules into various types of charged particles such as electrons, cations, anions, free radicals and even some metastable products like atoms etc. In accordance with a report by Schriver and group, non-equilibrium plasma is a low-pressure one featuring higher temperature of electrons compared to that of heavy species i.e. ions and neutrals. Consequently, the Maxwell-Boltzmann velocity distribution for the electrons differs from the same for the ions [**40**]. Whilst, on placing plasma in a closed system, a state of thermodynamic equilibrium can be attained and maintained between each phenomenon and its reverse counterpart such plasmas are usually referred to as equilibrium plasma and are characterized by high number densities and temperatures of each species- including both the electrons and heavy particles. The corresponding radiation corroborates with black-body radiation attributes and can be described using Planck's radiation law. The non-equilibrium plasma is electrically composed of both AC and DC systems. The related equipment is also configured as transferred and non-transferred ones [**41],[37**].

Plasma treatments may also be categorized based on the nature of process gas used or on the conditions of application. Techniques using industrial oxygen as a process is used for the treatment are termed as 'oxygen plasma'. While those, using aerial oxygen are referred to as 'atmospheric plasma'. Oxygen is the most widely used process-gas, although any gas may be applicable for this purpose. On the basis of operational conditions, plasma treatments can be further classified such as 'vacuum plasma'- the treatment which is conducted under a controlled condition inside a sealed chamber maintained at a medium level of vacuum. Plasma treatments performed under conditions of low temperatures are thus termed as 'cold plasma'. However, the term "plasma treatment" is a general one which is applicable to vacuum plasma treatment. But, technically other methods like atmospheric plasma and corona are also considered to be plasma treatments as well [**42, 43**]. Individually, all of these types differ from each other in terms of their characteristics, depths of treatment and the chemical action on the surface of the substrate. A group of researchers studied the application of activated-gas plasma treatment on numerous polymers [**44**]. Another report focussed on some other non-conventional polymers including nylon 11, nylon 6/12, nylon 12, polyarylsolfone, polyethersulfone, polyphenylene sulfide, polybutyl terephthalate polyester and ECTFE fluoropolymer. Some more works involving plasma treatment on polymers could be referred to from the following references **[45-55]**.

2.2.6.1. Corona Treatment

A type of non-equilibrium plasma is Corona discharge, which is an electrical discharge an outcome of weak ionization of air in the close neighbourhood of an electrically charged conductor [**56-58**]. The generation of corona discharge can be accomplished by using a strong and continuous DC electric source often posing the requirement of a single electrode. The corona discharge technology differs subtly from the low-temperature plasma by the fact that the former occurs at normal atmospheric pressure, while the later has negligible pressure requirement or vacuum. Corona discharge phenomenon is also at times referred to as a 'double-edged sword' owing to its dual natured consequences- both favourable and unfavourable. Inspite of associating with a number of shortfalls such as-power loss, noise, signal interferences and damage caused to insulation [**59-60**], corona discharge has been outstanding with its unparalleled scientific, commercial and industrial applications [**61**]. Majority of the investigational studies on corona discharge are experimental, rather than theoretical.

The most widespread and efficient, hitherto, technique of surface modification has been the Corona treatment method that is extensively used in the packaging sector. Olefinic polymer films used for packaging are corona treated so as to result in an enhanced surface adhesion and printability. The method involves the application of a low-energy electric voltage (10-40 kV) operating at a high frequency range (1-4 kHz) to the surface of a polymeric film moving between an electrode and a roller [**62**].The electrical energy leads to the ionisation of the air molecules present between the electrode and the surface of the moving polymer, thereby generating excited species (electrons, ions, radicals or molecules) which subsequently get incorporated onto the polymeric surfaces by means of surface adsorption (chemisorption). As such, the incorporation of polar functionalities onto the surface of polymer enhances its adhesion and wetting characteristics. The detection of polar functional groups such as -OH, -COOH, -C=O and $-C{=}ONH_2$ on polyolefinic surfaces has been made using XPS findings following corona treatment **[63-64]**. Reports have concluded that some key factors that need to be precisely controlled in order to bring out good adhesion characteristics to polymeric surfaces include- the voltage and frequency of the source field, the time of exposure, the composition of the gas atmosphere and the geometry of the sample and/or the electrode **[65-66]**. The following references would throw more light on various works involving corona treatment on different polymers **[67-80]**.

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Chapter 3:

MATERIALS AND METHODS

3. MATERIALS AND METHODS

This chapter gives details of all the materials used in the present study along with the methods of characterization of the LD/LLDPE films undergoing corona treatment at different wattages of different structures and compositions. A brief description of the process for fabrication of films has been given which includes the physical parameters of the co-extruder maintained during the processing of the three-layered composite films. The composition of each layer and the technical data of all the different granules have been documented so that a plausible concept can be envisaged about the rheological aspects of the films. A brief narration of each of the methods of characterization of the films before and after the Corona treatment has been given along with the pictorial representation of the equipments used for the specific purpose, wherever possible. In about all the cases standard procedures of testing as per either ASTM (American Society for Testing and Materials) or BS (British Standards) had been followed excepting a few cases where testing methods have been improvised so as to explain some specific characteristics of the films and the laminates thereof. However, the results obtained in such cases had been corroborated with the earlier findings and the results available in literature.

3.1. Structure and Composition of the Three-layered Co-extruded LD/LLDPE Film (for Transparent and Opaque films)

3.1.1. Physical Properties of the LD/LLDPE Granules Used

Transparent and milky white polyethylene films were fabricated by using the technique of co-extrusion. A 75 μm thick film consisting of three layers of equal thicknesses was designed using LD/LLDPE blends. The mixing ratio of different grades of LLDPE and LDPE varied layer to layer. In the three-layered co-extruded films, the first one (also called the sealant layer) was composed of LDPE and different grades of LLDPE where both the virgin polymers contained a certain fraction of slip additive having the trade name EURECAMIDE, an amide containing chemical compound. The first layer was the one which was designed to come in direct contact with the product and was the innermost layer of the bubble formed during fabrication of the blown film by means of co-extrusion process. The middle and the third layers were devoid of slip additives. The details of composition and the source of the different plastic raw materials are given below in table-3.1, 3.2.

Fig-3.1: Different grades of PE granules that were used for the fabrication of the LD/LLDPE Co-extruded (Both Transparent and Opaque) films.

The grades of polyolefins and film thickness adopted for the study were in compliance with the mostly recommended ones applicable for packaging and refrigerating raw food products like fresh meat and vegetables. The fabrication of the blown films, involved the mechanism of co-extrusion characterized by a blow-up ratio (BUR) of 2.78:1 having 300 mm die sizes with 2.2 mm lip gap. The films were run at a line speed of 13.1 m/min and the extruder screws, all having 55 mm outer diameter (O.D.)were rotated at a speed of 80 rpm. The formed bubble of the blown film was immediately made to collapse at a deformation board, where corona treatment of the third (outer) layer was carried out in-line by a Corona Treater of IEEC brand, with a maximum capacity of 5.0 kW applied load.

Table-3.1: Composition of the Transparent Co-extruded LD/LLDPE films

Layer	Composition			Mixing Ratio	MFI	Density	Slip
	Grade	Supplier	Nature of Polyethylene				
1st Layer / Inner layer (Sealant Layer)	Octane O21010	Reliance (India)	LLDPE	25:25:8=3:3:1	0.90	0.918	√
	Exceed 1018 JA	Exxon Mobil (Singapore)	Metallocene LLDPE		1.00	0.918	√
	Sabic HP 0323N	SABIC (Saudi Arab)	LDPE		0.30	0.923	√
2nd Layer (Middle Layer)	Octane O19010	Reliance (India)	LLDPE	25:25:8=3:3:1	0.90	0.918	×
	Butene F19010	Reliance (India)	LLDPE		0.90	0.918	×
	Relene 1005FY20	Reliance (India)	LDPE		0.50	0.920	×
3rd Layer / outer layer (Corona Treated Layer)	Exceed 1018 KA	Exxon Mobil (Singapore)	LLDPE	25:25=3:3	1.00	0.918	×
	Relene 1005FY20	Reliance (India)	LDPE		0.50	0.920	×

For the opaque white film, the same blend of polymers had been used across all the three layers. The second and third layer both consisted of a white master batch in order to impart the adequate level of opacity to the fabricated film. The first layer, having the sealing characteristics, was meant to come in contact with the packaged product (the innermost one) were loaded with a certain level of slip additive EURECAMIDE.

Table-3.2: Composition of the Opaque Co-extruded LD/LLDPE films

Layer	**Composition**			**Mixing Ratio**	**MFI (g/10min)**	**T_g (° C)**	**T_m (° C)**	**Density (g/cm³)**	**Slip**	**Non-Slip**
	Grade	**Supplier**	**Nature of Polyethylene**							
1st Layer (Inner Layer) Sealant Layer	Exceed 1018 KA	Exxon Mobil (Singapore)	mLLDPE	50:8:0.1	1.00	---	247	0.918	√	×
	Relene 1005FY20	Reliance (India)	LDPE		0.50	-130	104-115	0.920	√	×
	Slip Additive	Plastiblends (India)	LD/LLDPE		38.5	---	---	0.915	√	×
2nd Layer (Intermediate Layer)	Octene O19010	Reliance (India)	LLDPE	20:30:8:4 = 5:7.5:2:1	0.90	-110	115-135	0.918	√	×
	Exceed 1018 KA	Exxon Mobil (Singapore)	mLLDPE		1.00	---	247	0.918	√	×
	Relene 1005FY20	Reliance (India)	LDPE		0.50	-130	104-115	0.920	√	×
	WMB 04012LL	Plasti Blends (India)	LD /LLDPE		20.70	----	--	1.20	√	×
3rd Layer (Outer Layer) Corona Treated Layer	Octene O21010	Reliance (India)	LLDPE	15: 8: 35: 4	0.90	-110	115-135	0.918	×	√
	Relene 22FA002	Reliance (India)	LDPE		0.20	-130	104-115	0.920	×	√
	Butene F18010	Reliance (India)	LLDPE		0.90	-110	115-135	0.918	×	√
	WMB 04012LL	Plasti Blends (India)	LD /LLDPE		20.70	---	--	1.20	×	√

3.2. Lay-out of the Extruder Used and Operating Conditions Maintained

Right after the formed bubble of the blown film was immediately made to collapse at a deformation board, the corona treatment of the outer layer was carried out in-line by a Corona Treater of IEEC brand, with a maximum capacity of 5.0 kW applied load.

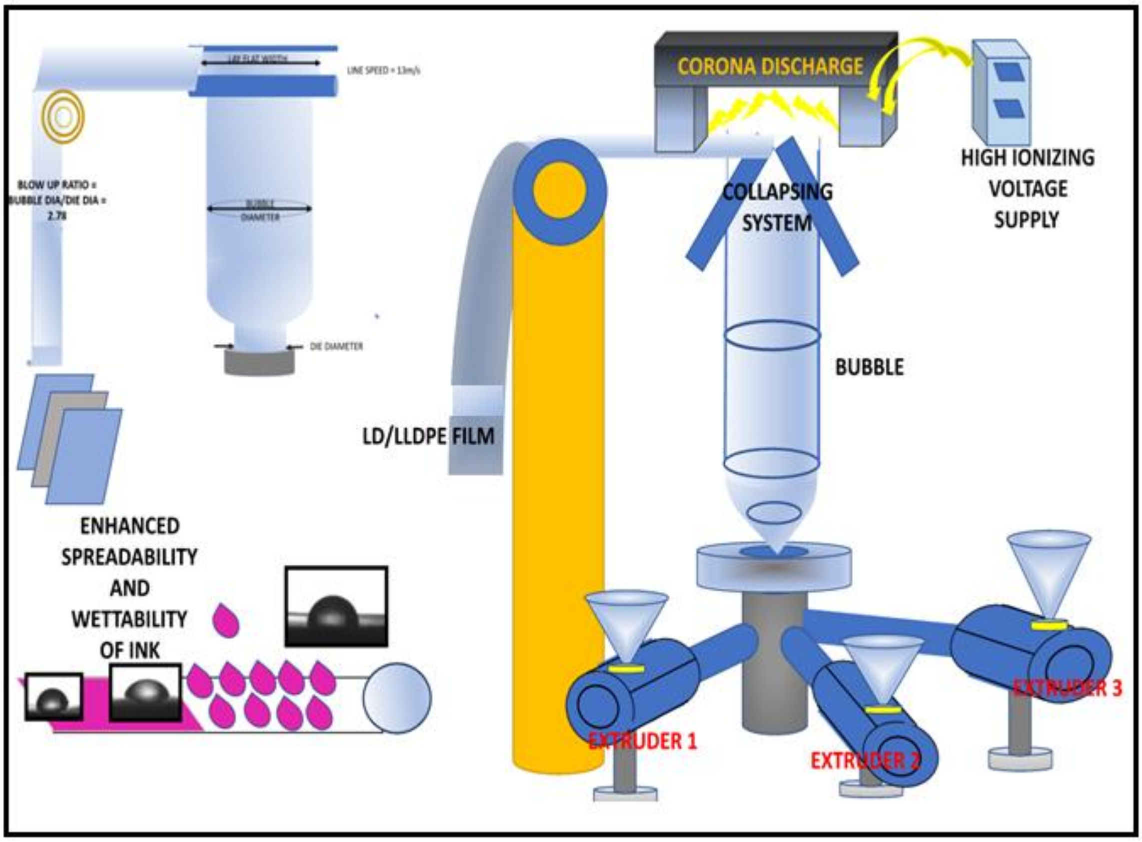

Fig-3.2: Pictorial representation of the fabrication process of the blown film and the subsequent in-line Corona Treatment on one side of the co-extruded LD/LLDPE film

The strong ionizing radiations coming out of the beam source had generated certain physical undulations over the plastic film surface, along with the introduction of certain polar functional groups, both factors being responsible for enhancing the plastic’s surface characteristics.

3.3. Brief Description of the Corona Treatment Process

The corona treatment process is an atmospheric pressure method used to modify the surfaces of plastics. It involves the application of an air electric discharge to enhance the surface properties of polymer films. In an extrusion line for films, the corona process is typically employed in-line before printing. The process consists of a power supply and a treatment device. The power supply converts standard utility power into higher frequency power, which is then supplied to the treatment device. The treatment device consists of two electrodes, one at high potential separated from the substrate surface by an "air gap," and the other electrode at ground potential, typically the surface on which the substrate is placed.

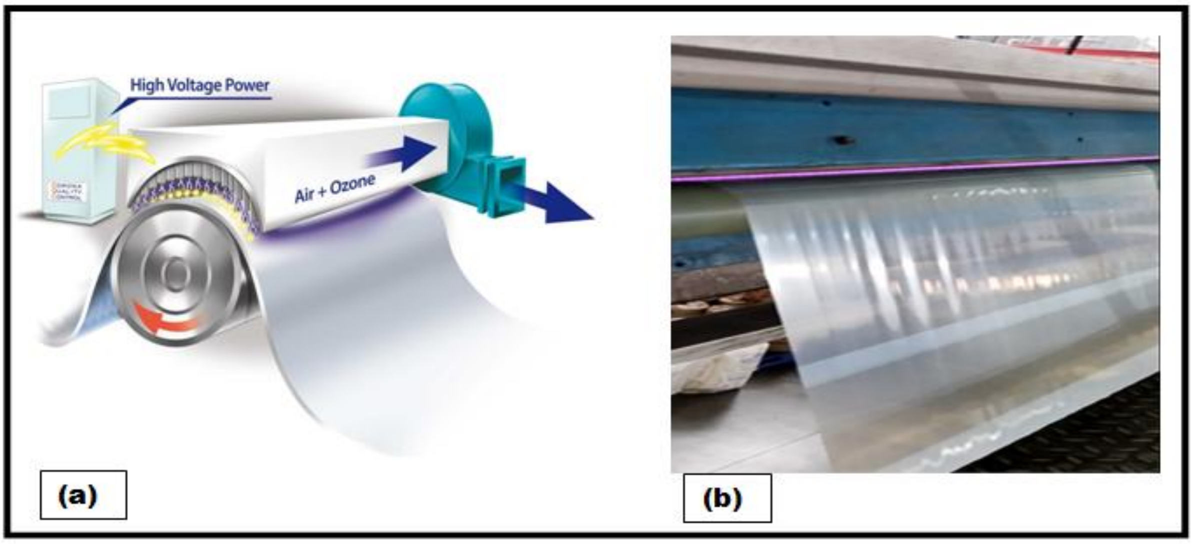

Fig-3.3: (a) Pictorial representation of the Corona Treatment on a plastic film (b) The photograph of the process as-fabricated in the present study

3.4. Methods of Surface Characterisation of the LD/LLDPE Films (both Transparent and Opaque)

3.4.1. Determination of Surface Energy

As per the primary motto of the thesis, surface adhesion of LD/LLDPE films was the central focus. The determination of surface tension of the corona treated films (co-extruded three-layered transparent LD/LLDPE film and co-extruded three-layered milky white LD/LLDPE film) have been carried out as per the ASTM D 2578–67 **[1]** standards. Standard solutions prepared by mixing different volume percentages of ethyl cellosolve and formamide and possessing different surface energies were separately applied on the corona treated side of films and the surface adhesion was investigated by observing spreading characteristics for a span of 2 seconds.

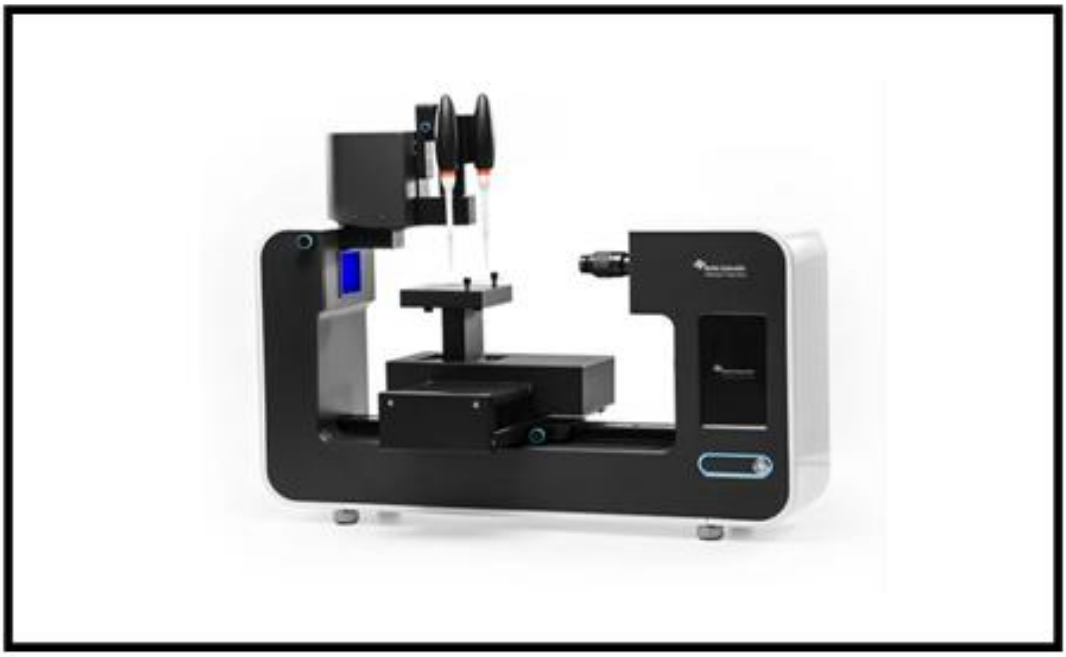

Fig-3.4: Digital Goniometer- Taken from Biolin Scientific

The surface tension determination of the corona treated side of the LD/LLDPE (both transparent and opaque) films was as per the mentioned standard accomplished by the surface energy value of the specific reference solution (mixture of ethyl cellosolve and formamide) which was found to form a stable liquid film over the treated surface for the mentioned duration, devoid of any droplet forming tendency. These observations were supported by the contact angle measurements by using a Goniometer. The contact angle subtended by a droplet of deionized water was calculated for this purpose. Additionally, the use of nitrogen plasma was also employed for the surface modification in one of the samples for the sake of conducting a comparative study.

3.4.1.1. Dyne Solution Method

A set of standard wetting solutions possessing different surface energies were prepared in accordance with ASTM D 2578–67 **[1]** for the purpose of determination of surface adhesion characteristics of the LD/LLDPE surface (before and after corona treatment for both transparent and opaque films). Different proportions of ethylene glycol-monoethyl ether (ethyl cellosolve) and formamide were mixed to produce solutions having a wide range of surface energies.

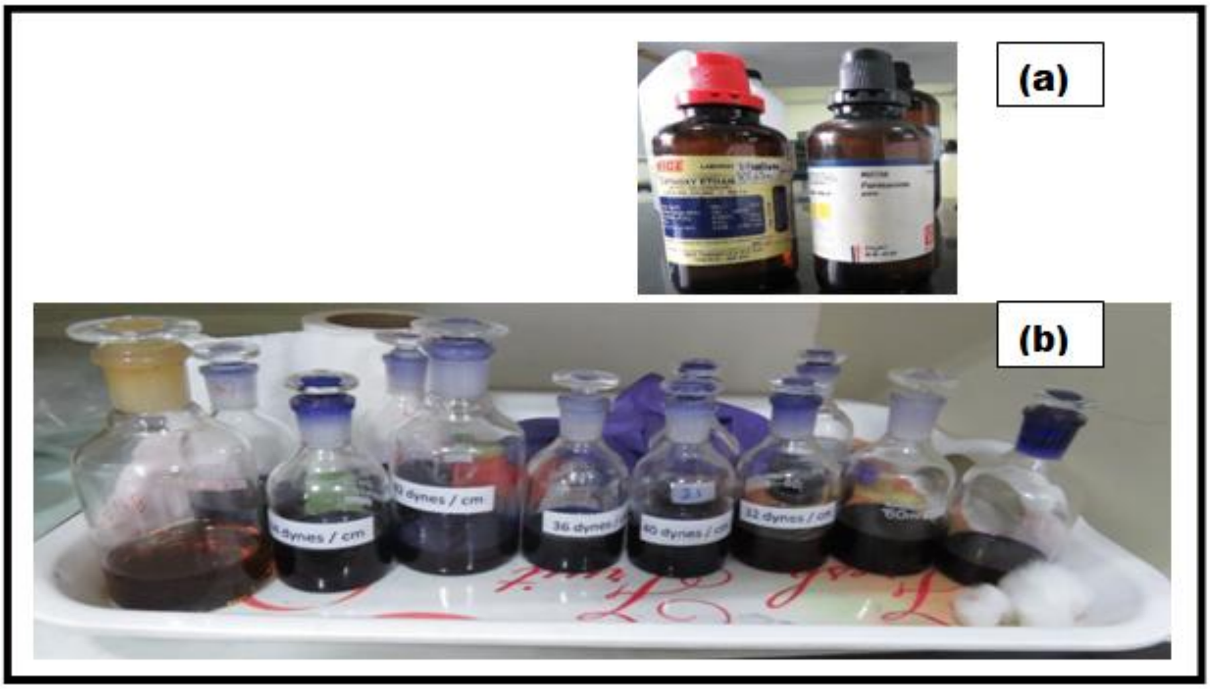

Fig-3.5: Pictures of (a) the solvents and the (b) as-prepared Dyne solutions used for the experiments

The following table consists of the different volume proportions of the components and the corresponding surface tension of the resulting mixture.

Table-3.3: Composition of the Wetting Solutions as per ASTM D 2578.

Volume of Formamide (cc)	Volume of Ethyl Cellosolve(cc)	Wetting Tension (dynes/cm)
0	100	30
2.5	97.5	31
10.5	89.5	32
19.0	81.0	33
26.5	73.5	34
35.0	65.0	35
42.5	57.5	36
48.5	51.5	37
54.0	46.0	38
59.0	41.0	39
63.5	36.5	40
67.5	32.5	41
71.5	28.5	42

Volume of Formamide (cc)	Volume of Ethyl Cellosolve(cc)	Wetting Tension (dynes/cm)
74.7	25.3	43
78.0	22.0	44
80.3	19.7	45
83.0	17.0	46
87.0	13.0	48
90.7	9.3	50
93.7	6.3	52
96.5	3.5	54
100.0	0	56

A comparative study was made to investigate the mode of changes in equilibrium contact angle made by a drop of de-ionized water on the surface of an untreated film of identical thickness vis a vis the equilibrium contact angles achieved on the surfaces of films which were treated at different wattages and the consequent surface energies obtained by applying standard wetting solutions. An untreated film of identical thickness was fabricated under identical conditions in the same extruder and was subjected to plasma treatment off–line in an atmospheric pressure plasma treater. The equilibrium contact angle of deionized water film on such plasma treated film was measured and reported. The wetting by deionized water film was observed to be maximum with the plasma treated film. However, this most modern method of surface modification is the most effective one [**2,3**].

3.4.1.2. Measurement of Contact Angle by Goniometer

The contact angle with deionized water on the surface of the treated LD/LLDPE film surfaces (both transparent and opaque) were measured by a Goniometer. Nitrogen Plasma was also used for the surface modification of the polyethylene films under investigation **[4,5,6].**

3.4.2. Scotch-adhesion Test

The efficacy of the surface adhesion of the corona treated films was evaluated by a standard scotch adhesive tape method by following the test method as per ASTM D 903: 98 (RA 2010) **[7].** A 15 mm width adhesive tape, that was procured from the market manufactured by M/s. 3M India Limited which was branded as Scotch Magic Tape, was adhered to the side possessing the surface treatment of the sample films by the application of mild finger pressure. An UTM (Universal Testing Machine) was used to measure the force, expressed in gmf/15 mm, to separate the scotch adhesive tape from the surface of the treated film. The required force is considered to be a measure of the extent of the treatment. A higher value of force represents a greater surface tension at a certain level of surface treatment. The peel adhesion strength increased proportionately with the treatment level.

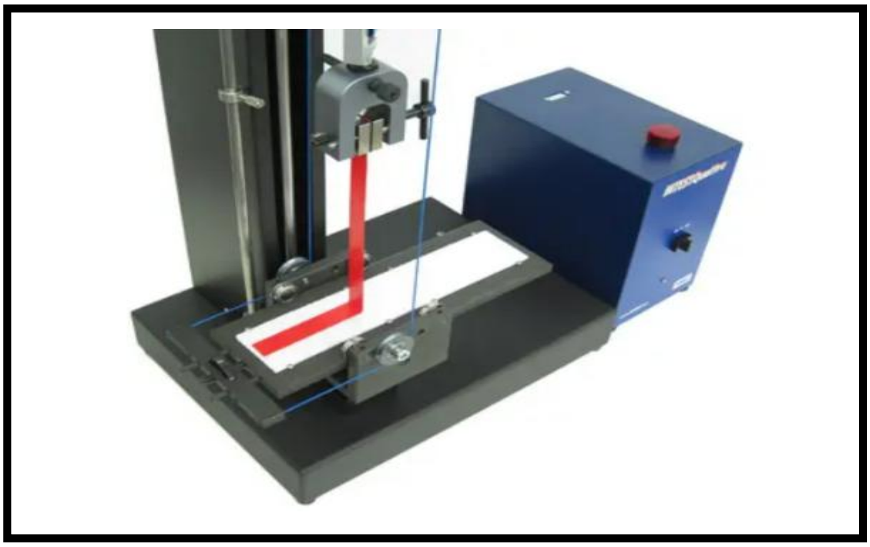

Fig-3.6: The set up of the Scotch-adhesion Testing

3.4.3. Measurement of Surface Roughness

The procedure outlined in ASTM D 1894–14 **[8]** was followed for the determination of coefficient of friction. Both static and kinetic coefficient of friction characteristics were evaluated on the corona treated surface of co-extruded film samples. This standard specifies a method for determining the coefficients of starting and sliding friction of plastic film and sheeting when sliding over itself or other substances. The standard provides guidelines for conducting the test, including the apparatus required, test specimen preparation, conditioning, and the procedure to be followed. The standard applies to non-sticky plastic film and sheeting with a thickness of up to approximately 0.5 mm. It is primarily used for quality control purposes and does not provide a comprehensive assessment of machinability. The test device consists of a horizontal test table, a slab, and a driving mechanism to produce relative motion between the slab and the test table. The test table should have a flat and smooth surface made of a non-ferromagnetic metal. For each measurement, two test specimens measuring about 80 mm x 200 mm are required. At least three pairs of test specimens, taken from points uniformly distributed over the width of the sample, should be tested. Unless specified otherwise, the test specimens should be conditioned for at least 16 hours in a standard atmosphere prior to testing.

Fig-3.7: The photograph of the Coefficient of Friction testing instrument (At the Indian Institute of Packaging, Kolkata) used in the measurement of surface roughness.

The below segment provides detailed instructions for conducting the friction test, including fixing the test specimens on the test table, initiating the motion, recording the forces involved, and determining the static and kinetic coefficients of friction. The frictional force acting during the sliding motion often differs from the constant value which characterizes the static friction. The kinetic coefficient of friction is determined by measuring the average value of the frictional force during the sliding motion. The kinetic coefficient of friction (μ_d) is given by the equation:

$$\mu_d = F_d / P \qquad [9]$$

where : F_d is the dynamic frictional force, expressed in newtons.

The force required to overcome the friction is recorded using a chart recorder or an equivalent electrical data-processing unit. For each measurement, the static coefficient of friction (μ_s) is calculated by dividing the static frictional force (F_s) by the normal force (P). The average value of μs is then determined from the results of multiple tests. For each measurement, the kinetic coefficient of friction (μ_d) is calculated by dividing the dynamic frictional force (F_d) by the normal force (P). The average value of μ_d is determined from the results of multiple tests. The coefficients of friction are typically expressed as dimensionless values ranging from 0 to 1, where lower values indicate lower friction and higher values indicate higher friction. Static coefficient of friction at any applied voltage remains always higher than the dynamic coefficient of friction at the corresponding applied voltage.

3.4.4. Fourier Transform Infrared (FTIR) Spectroscopic Studies

FTIR spectroscopy is a widely used technique for analyzing how materials interact with infrared light. It involves observing the characteristic vibrations that occur when infrared light collides with molecules. This technique provides information based on the chemical bonds present in the sample. The key component of FTIR spectroscopy is the Michelson interferometer, which allows for the simultaneous exposure of the sample to multiple frequencies of infrared light. The transmitted light is then processed and compared to a reference sample using a Fourier transform to obtain the complete spectrum.

FTIR spectroscopy offers several advantages over traditional dispersive techniques. It collects information from all wavelengths at once, resulting in reduced noise and faster measurements. This technique finds widespread applications in various fields such as the analysis of carbon-containing organic compounds, polymer characterization, forensic analysis, pharmaceutical analysis, and food testing. By examining the characteristic peaks in the IR spectrum, it is possible to identify the composition of a sample and detect any deviations from expected spectra, indicating contamination or changes in materials. FTIR, or Fourier transform infrared, is a widely used spectroscopic technique that investigates the interactions between specimen under investigation and infrared radiation. It operates by passing infrared radiation through a sample and measuring the absorption of specific wavelengths by the sample's molecules. The remaining transmitted radiation is then analyzed. Through the absorption of infrared radiation at characteristic frequencies, different molecules and functional groups produce unique spectra. Compared to older spectroscopic methods, FTIR offers advantages in terms of speed, precision, and non-destructiveness.

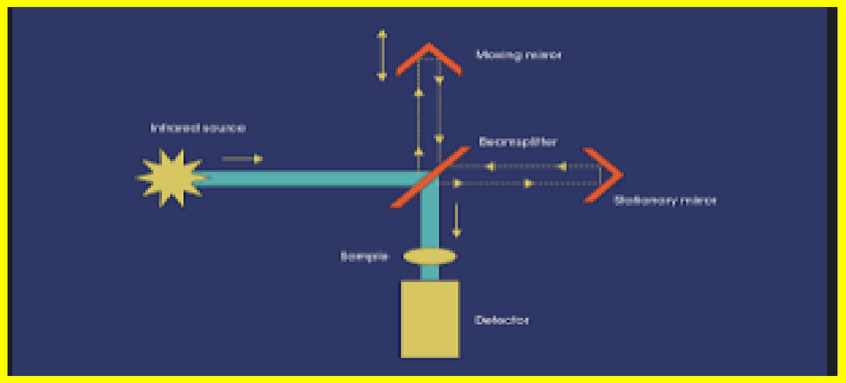

Fig-3.8: The pictorial representation of the working of FTIR instrument

These benefits are achieved using an interferometer as the infrared source, which generates an interferogram—a graph depicting the intensity of radiation over time. By applying the mathematical process known as Fourier transform to the interferogram, the spectrum is obtained by breaking it down into its constituent frequencies, resulting in the recognizable FTIR spectrum. ATR spectroscopy is particularly useful for studying thick or multilayered samples like paints, rubbers, plastics, and coatings.

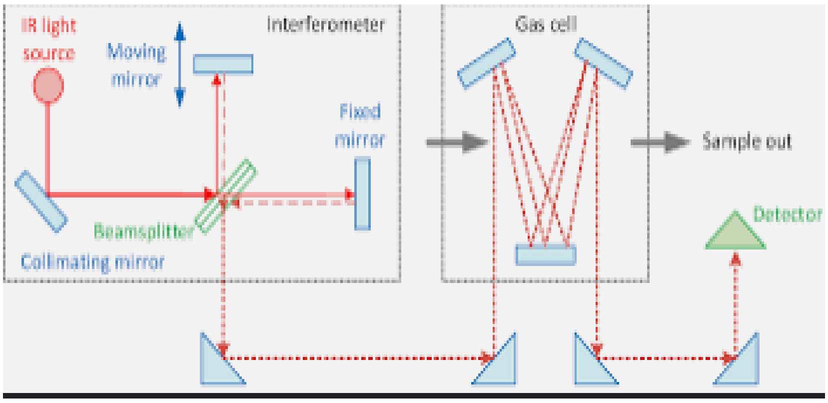

Fig-3.9: The pictorial representation of the working of FTIR instrument-ATR mode

Fig-3.10: The photograph of an FTIR Instrument

3.4.5. Morphological Studies by Scanning Electron Microscope (SEM)

A scanning electron microscope (CARL ZEISS EVO,18, Special edition, Germany) was used to determine the topography of the treated film samples after necessary gold sputtering. An accelerating voltage of 15 kV was used.

Fig-3.11: The photograph of a CARL ZEISS EVO SEM Instrument

3.5. Determination of Heat-seal Joint Strength

The heat-seal joint strength was determined following the procedure outlined in ASTM F 88 **[10].** Sealing was carried out in an impulse sealer for a dwell time of 0.9 sec. Samples of 15 mm were punched and tested in UTM.

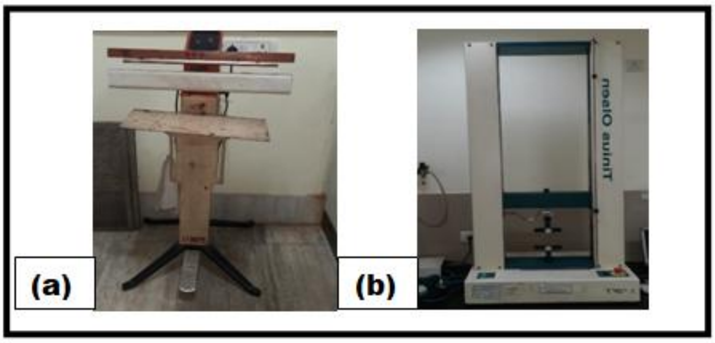

Fig-3.12: The photograph of the (a) Heat Sealing machine and (b) the Universal Testing Machine (At the Indian Institute of Packaging, Kolkata, India) used in the Heat-seal joint strength determination.

3.6. Determination of Mechanical Properties of LD/LLDPE Films (both Transparent and Opaque)

Elastic modulus, yield stress, peak stress, % EB, and tensile energy absorption (TEA) of the treated films were determined as per ASTM D 882 **[11].** The dart impact test and tear resistance (Greaves Tear) test were done as per ASTM D 1709 and ASTM D 1004 **[12]**, respectively.

Fig-3.13: The photograph of the Dart Impact Tester (At the Indian Institute of Packaging, Kolkata, India).

3.7. Determination of Barrier Properties of LD/LLDPE Films (both Transparent and Opaque)

3.7.1. Determination of Water Vapor Transmission Rate (WVTR)

WVTR (water vapor transmission rate) refers to the rate at which water vapor permeates through a film under specific temperature and relative humidity conditions. It is measured in g/100 in^2/24 hr in US standard units and g/m^2/24 hr in metric (SI) units. Exxon Mobil has established 100°F (37.8°C) and 90% RH as the standardized test conditions for WVTR, which are commonly reported. ASTM F1249 standard **[13],** titled "Standard Test Method for Water Vapor Transmission Rate through Plastic Film and Sheeting Using a Modulated Infrared Sensor." This standard provides a procedure for determining the rate of water vapor transmission through flexible barrier materials such as plastic films and sheets. The key points on the test procedure are mentioned in the text below.

The test method covers the measurement of water vapor transmission rate (WVTR) through flexible barrier materials. It is applicable to sheets and films up to 3 mm (0.1 in.) in thickness, including single or multilayer synthetic or natural polymers and foils, including coated materials. The method provides for the determination of WVTR, the permeance of the film to water vapor, and the water vapor permeability coefficient for homogeneous materials.

Provides definitions of key terms used in the standard, including water vapor permeability coefficient, water vapor permeance, and water vapour transmission rate. The procedure for measuring WVTR involves a diffusion cell and a pressure-modulated infrared sensor.

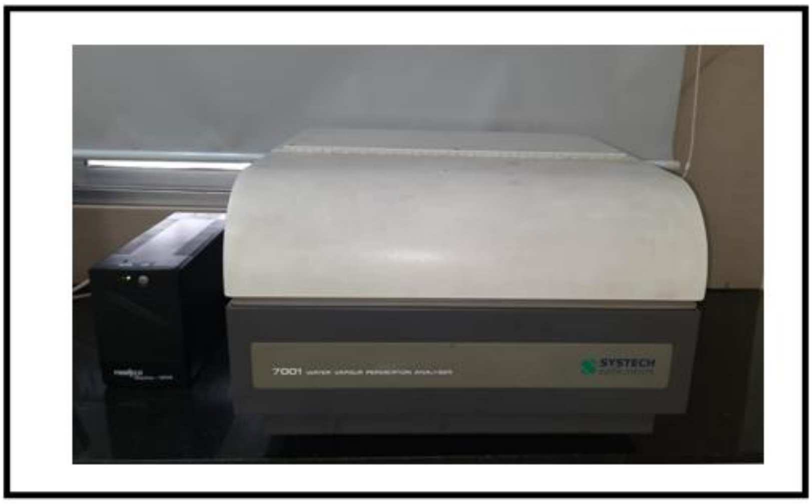

Fig-3.14: The photograph of the WVTR instrument (At the Indian Institute of Packaging, Kolkata, India) used in the Barrier property determination.

Water vapour diffusing through the film is measured by the sensor, and the WVTR is calculated based on the electrical signal produced. The test method is used to obtain reliable values for WVTR, which is an important property of packaging materials related to shelf life and product stability. The test method involves evaluating a barrier material to determine its ability to transmit water vapor. It utilizes two chambers, namely a dry chamber and a wet chamber, which are separated by the material under investigation. This arrangement creates a diffusion cell. Water vapor passes through the test film and mixes with the gas present in the dry chamber. The resulting vapor is directed to a pressure-modulated infrared sensor. This sensor measures the proportion of infrared energy absorbed by the water vapor and generates an electrical signal. The magnitude of this signal is directly proportional to the concentration of water vapor. To evaluate the performance of the test film, its electrical signal is compared to that produced by a calibration film with a known water vapor transmission rate. By analyzing the difference in signal amplitudes between the test film and the calibration film, the rate at which moisture permeates through the tested material can be determined.

3.7.2. Determination of Oxygen Transmission Rate (OTR) Properties

OTR, which stands for oxygen transmission rate, is a measurement that quantifies the speed at which oxygen gas permeates through a film under specific temperature and relative humidity conditions. It is a crucial parameter for evaluating the performance of packaging materials. OTR values are commonly expressed in units such as cc/100 in²/24 hr (US standard units) or cc/m²/24 hr (metric or SI units).The significance of OTR lies in its direct impact on the preservation of oxygen-sensitive products. Although oxygen is essential for life, it can also contribute to food spoilage and degradation.

Fig-3.15: The photograph of the OTR instrument (At the Indian Institute of Packaging, Kolkata, India) used in the Barrier property determination.

To minimize oxygen exposure, two primary methods are usually employed:

Modified atmosphere packaging (MAP): This method involves replacing the air in the package's headspace with an alternative gas, such as nitrogen or a mixture of nitrogen and carbon dioxide, before sealing. It is widely used to extend the shelf life of various products, including potato chips, dried fruits, nuts, and shredded cheese.

Vacuum packaging: In this approach, the package is evacuated of air, creating a vacuum inside and causing the flexible packaging to conform closely to the product shape. Meats (both fresh and processed) and cheeses are commonly packaged using this technique. After the air has been replaced or eliminated, maintaining a low oxygen concentration within the package requires utilizing a film with effective oxygen barrier properties and reliable sealing. OTR values serve as a means to compare the oxygen barrier capabilities of different packaging films. As a general guideline, materials with an OTR of less than 1 cc/100 in²/24 hr (or 15.5 cc/m²/24 hr) are considered to have a "high oxygen barrier." In accordance with the standard, a procedure for determining the steady-state rate of oxygen gas transmission through various types of plastic materials, including films, sheets, laminates, co-extrusions, and plastic-coated papers or fabrics. The test method covers the measurement of oxygen gas transmission rate (O_2 GTR), permeance of the film to oxygen gas (P_{O_2}), and oxygen permeability coefficient (P'_{O_2}) for homogeneous materials.

An amount of a given gas (oxygen) is allowed to pass through a unit of parallel surfaces (one placed on top of another) of a plastic film in unit time under the conditions of test. The test conditions to be maintained include temperature, partial pressure, relative humidity and hydrostatic pressure of the gas (oxygen) on both sides of the film.

Fig-3.16: The photograph of the Manometric Gas Transmission Cell which operates within an OTR machine.

The procedure as per ASTM D 1434 **[14]** involves mounting of the sample in a gas transmission cell in such a way that a sealed semi-barrier is created in between the two chambers. One of the chambers contains the test gas, i.e. oxygen in our case, maintained at a specific high pressure, while the other chamber, being maintained at a lower pressure, is designed to receive the permeating gas. Two different methods are available, as discussed below:

Procedure M— In this procedural method, the lower pressure chamber is at first evacuated and the gas transmission occurring through the sample is denoted by an increase in pressure.

Procedure V—In this procedural method, the lower pressure chamber is operated at near atmospheric pressure and the gas transmission through the sample is depicted by a volume change.

3.8. Determination of Opacity of the Opaque LD/LLDPE Films

Opacity is an important optical characteristic of film that is measured based on reflectance ratios. Various factors such as thickness, filler content, fiber bleaching, coating, etc., influence the opacity of the film. The principle behind determining opacity is as follows:

The sample under investigation is combined with a white backing, its reflectance is higher compared to when combined with a black backing. This is because light transmitted through the partially opaque sheet is mostly reflected by the white backing, and a portion of the light is transmitted through the plastic again, increasing the overall reflection. Two types of "white" backings are used, resulting in two measures of opacity: Opacity (89% reflectance backing), also known as contrast ratio ($C_{0.89}$), is calculated as 100 times the ratio of the diffuse reflectance (R_0) of a specimen backed by a black body with a reflectance of 0.5% or less to the diffuse reflectance ($R_{0.89}$) of the same specimen backed by a white body with an absolute reflectance of 89%. Hence, $C_{0.89} = 100\ (R_0/R_{0.89})$. Perfectly opaque plastic has a contrast ratio of 100%, while perfectly transparent sheets have only a few percent contrast ratio. Opacity, also referred to as printing opacity, is calculated as 100 times the ratio of the light reflected by a plastic specimen when backed by a black body with a reflectance of 0.5% or less (R_0) to the light reflected when the specimen is backed by a thick stack of the same plastic (R_∞). Therefore, opacity (paper backing) = $100\ (R_0/R_\infty)$**[15].**

To summarize, opacity of plastic is determined by comparing reflectance ratios obtained with different backing materials—a white backing and a black backing. The measurements reflect the extent to which light is reflected or transmitted through the plastic, and higher opacity is desired for certain applications. The test method is based on the Indian Standard IS/ISO 2471:2008, **[16]** which is an adoption of the corresponding international standard ISO 2471:2008 issued by the International Organization for Standardization (ISO). The test method involves measuring the luminance factor of a single sheet of plastic over a black cavity and the intrinsic luminance factor of the plastic. The opacity is then calculated as the ratio of these two luminance factor values. To perform the test, specific apparatus is required, including a reflectometer with defined characteristics and calibration standards for photometric and UV adjustments. Calibration is emphasized to ensure accurate measurements. Opal glass or ceramic plates are recommended as working standards.

Fig-3.17: The photograph of the Konica Minolta Spectrophotometer (At the Indian Institute of Packaging, Kolkata, India).

3.9. Ageing Characteristics of Treated LD/LLDPE Film (Both Transparent and Opaque)

Small rolls of LD/LLDPE co-extruded treated films were put in a humidity cabinet maintained at a temperature of 40^{o}C ±2º C and 90% ± 2 % (RH) relative humidity under tight winding conditions **[17].** The spools used to be taken out at specified time intervals and samples were collected for measuring the treatment levels. The spools were further kept in the cabinet and samples were collected at the time intervals same as that in the first case for over 700-800 days.

Fig-3.18: The photograph of the Humidity Chamber (At the Indian Institute of Packaging, Kolkata, India) used in the Ageing Test.

Further studies on the fabricated LD/LLDPE coextruded films (both transparent and opaque) were carried out in subsequent works. In one such, the pre-treated LD/LLDPE coextruded films (the treatment levels being varied by applying different voltages) were coated with liquid gravure inks of different colours (different pigment being used, the other formulation remaining the same) with gravure cylinder having a screen size of 150 lines/cm in a commercial gravure printing machine and thoroughly dried by passing the coated film through a drying tunnel. In an endeavour to find how the inks of different colours interact with the polyolefinic surfaces with different surface charges and how the polarity of the new surfaces (the inked surfaces) thus created behave in turn during its subsequent processing as required and demanded by the necessities of suitable packaging specification, the corresponding studies had been undertaken. The different commercially used packaging films consist of monolayer and multilayers. In case of monolayer the single plastic film must have the dual characteristics of good integrated pilfer proof sealing and at the same time good printability. After packing the product the printed (inked) surface should have reasonably good surface polarity so as to provide the necessary anchorage towards the batch printing ink. In case of multilayer specification, the printed or inked surface must have the necessary charges or polarity so that there becomes no problem during application of adhesive (proper wetting and spreading are required here again) and subsequent lamination to the other films. All these are being carried out in the concerned industries in a haphazard manner and in a non-scientific manner such that they face various types of problem very frequently and tackle the issues by “Hit and Miss” policy for the moment itself. Thus we had tried to articulate a scientific document, the main purpose of which would enable the concerned industries to analyze the issues quite meticulously in a scientific manner. From the survey of literature, it was observed that no such works were conducted till date. Our aim was thus to provide the packaging and laminating industries a hassle free, easy and smooth day to day operation.

3.10. Printing Inks and the Process of Printing over the Treated Transparent LD/LLDPE Films

Liquid gravure inks exclusively suitable for printing on the surface of corona treated co-extruded Polyethylene films (LD/LLDPE) were procured from M/S. Sakata Inx (India) Private Limited. Three primary colour of inks (namely Yellow, Magenta and Cyan) and two secondary ink (black and white) were selected in order to investigate the influence of pigments (if any) on the adhesion characteristics of the dried ink film after getting suitably printed. The inks were of low viscosity (15-18sec) such that it can enter and fill the cells of the gravure cylinder very fast and at the same time possessing the unique characteristic of being released very quickly while in contact with the web of film under nip pressure and leave behind a thoroughly dried uniform ink film over the plastic surface after passing through the drying tunnel maintained at a temperature of 80-95 ºC by blowing hot air current through the tunnel. The inks were all identical excepting the colour (pigment) having the same medium and other additives. The solvents play a great role in preparing the inks and in diluting the inks to achieve the required low viscosity, an essential parameter of gravure inks. However, it is an added advantage that the organic solvents employed for the purpose of gravure inks have very low surface tension which help in wetting and spreading of the ink over the plastic surface.

Table-3.4: Details of Printing inks used from Sakata Inx (India) Private Limited:

Sl. No.	Name of Ink	Batch No	Manufacturing Date	Code
01	Magenta (Red)	0001174394	13.05.2023	Geranium – 350, PR-1
02	Cyan (Blue)	0001152667	27-02-2023	ARSR Blue 800
03	Yellow	0001183594	04-06-2023	ARSR Yellow 238
04	Black	0001145335	08-02-2023	ARSR 231000
05	White	0001176309	17.05.2023	ARSR White 102 - II-P022

3.11. Measurement of Coating Weights of Different Inks on Treated Transparent LD/LLDPE Films

Three samples, two from edges and one at the centre were collected from each inked (mother) film sample with the help of a template of specified dimension (10cm x 5cm). The sample was weighed in a digital balance which can weigh up to four decimal places. The ink film was then removed from the surface of the plastic film with the help of a cotton flock soaked in suitable solvent and rubbing it over the inked surface. Once the ink was completely removed, the sample was thoroughly dried in an oven maintained at a temperature of 105 ^{0}C and weighed further after cooling the sample to the room temperature. The difference between the two weights gives the coating weight of the ink film over the area of the template used for cutting the sample. This was then expressed in GSM or grams per square meter which is the conventional practice in industries. A gravure cylinder or annilox was etched in a manner so as to maintain the uniformity of coating throughout the entire web. The schematic presentation of the gravure printing machine, layout of an individual coating unit and a typical gravure cylinder is given in figure-3.19 c.

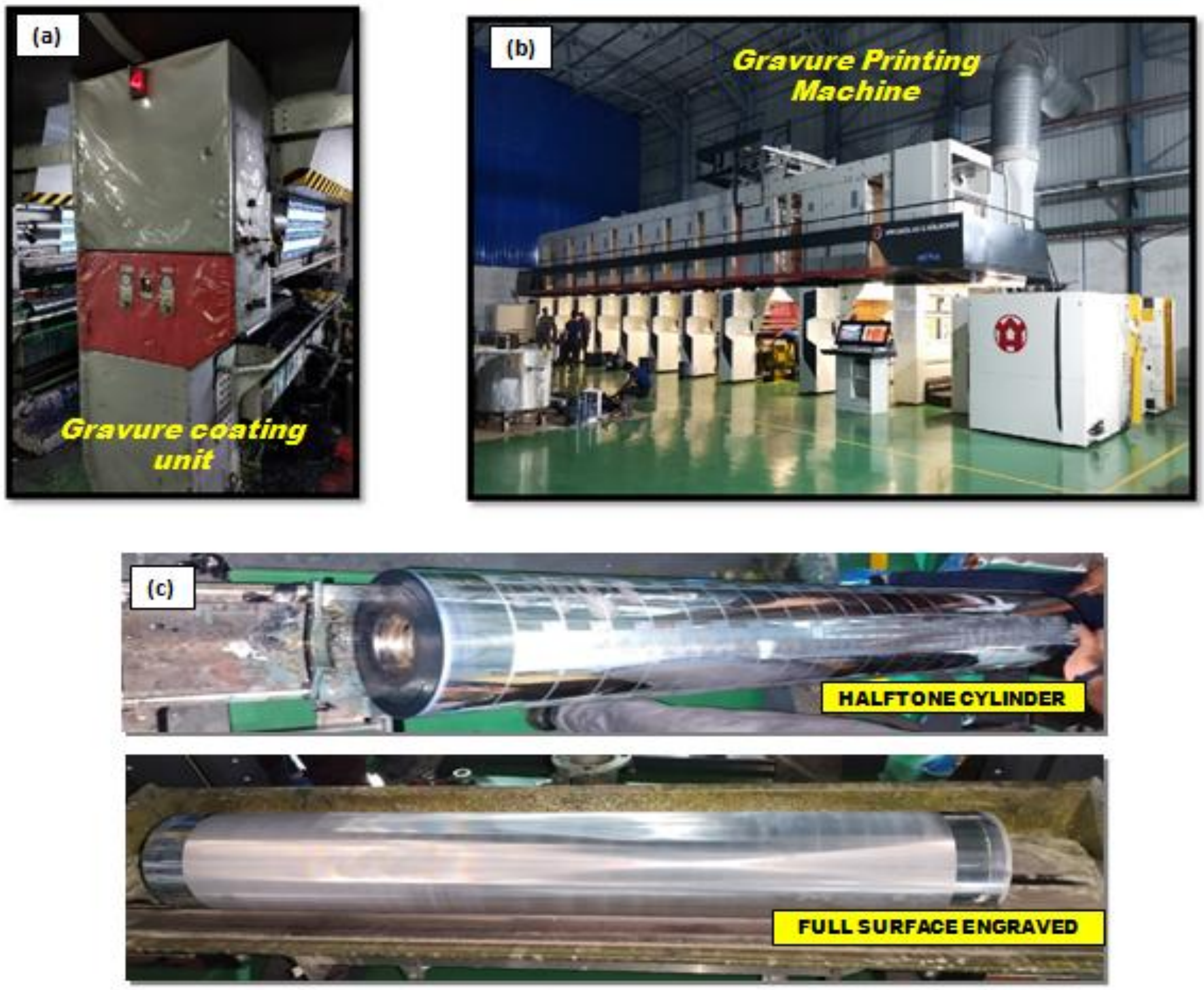

Fig-3.19: Pictures of (a) Gravure Coating Unit, (b) Gravure Printing Machine (c) typical Gravure Cylinder (Courtesy M/S. A.B. Poly Pack Pvt. Limited, Kolkata)

3.12. Determination of Surface Energy of the Bare Corona Treated Transparent LD/LLDPE Film after Printing with Inks of Different Colours

The surface energies of the corona treated (at different voltages or applied loads) films after printing with different colors were determined by following the standard procedure as outlined in ASTM D 2578–67 **[1]** using dyne solutions prepared by mixing ethyl cellosolve and formamide in different proportions as discussed in section 3.4.1.1.For the above mentioned pre-treated inked LD/LLDPE (transparent) films the following tests namely-roughness (coefficient of friction), mechanical properties, barrier properties, scuff proofness and ageing characteristics were also carried out as per standards which have already been mentioned previously in this chapter itself. The results of all tests are discussed in the following chapter.

3.13. Scuffing Characteristics of the Printed LD/LLDPE (Transparent) Treated Surfaces with Different Colours

The scuff proofness testing on the printed surface was carried out in two ways: 1) between the print surface and the unprinted surface and 2) between the two printed surfaces. This had been done as per ASTM F 2497 **[18]** with the PIRA Rub resistance tester.

Fig-3.20: Picture of PIRA Rub resistance tester (At the Indian Institute of Packaging, Kolkata)

In the last work it had been investigated how the corona discharge improves the spreading and wetting characteristics of printing inks or other coatings over the surface of LD/LLDPE co-extruded films. In the preceding attempt it was attempted to develop an idea how the surface charge over the printing ink film on the LD /LLDPE film surface which had already been corona treated at different kW loads so as to develop different levels of surface energies or tensions changes. In other words a quest had been made whether the initial level of surface energy (corona treatment imparted to the LD/LLDPE coextruded film at different wattages) had any influences on the resulting surface energies over the printed or coated surface. Further processing such as lamination with other substrates after application of adhesive over the ink film (in case of lamination where the ink film is sandwiched between the original film and secondary laminant film) is carried out or in case of surface printed jobs where some batch printing is necessary for every information of the product is laid down over the ink film itself. A few words about the normal practice followed in industry should be mentioned at this point. In case of lamination with reverse printed films as mentioned above the film which does not undergo any stretching or elongation under tension is usually printed, adhesive coated, thoroughly dried by passing the printed or coated film through a drying tunnel maintained at elevated temperature and then laminated or combined with the second substrate (film) relatively more stretchable one like LDPE or LLDPE coextruded film being already corona treated **[20].**

3.14. Printing Inks and the Printing Process on Treated LD/LLDPE Films

Liquid gravure inks most extensively used for printing on corona treated LD/LLDPE film surfaces were procured from the manufacturer, M/S. Sakata Inx (India) Private Limited, out of which, three were primary coloured inks (Yellow, Magenta and Cyan) and two were secondary inks (Black and Green). These inks were used in the investigation of lamination characteristics of various plastic films post application of ink coatings. All the inks were found to be of low viscosity (15-18 sec.) facilitating them to enter and fill the cells of the gravure cylinder quickly and simultaneously possessing the requisite characteristic of being capable of getting released instantaneously while staying in contact with the brisk moving web of plastic film under the normal operational conditions of nip pressure and at the same time leaving behind a completely dried, uniform ink coating layer over the plastic surface after drying at a temperature of 80-95 ºC. The properties of all the used inks were all similar barring their colour (pigment).

Table-3.5: Details of Printing Inks* used:

Sl. No.	Name of Ink	Batch No	Manufacturing Date	Code
01	Magenta (Red)	0001174394	13.05.2023	Geranium – 350, PR-1
02	Cyan (Blue)	0001152667	27-02-2023	ARSR Blue 800
03	Yellow	0001183594	04-06-2023	ARSR Yellow 238
04	Black	0001145335	08-02-2023	ARSR 231000
05	Green	0001176309	17.05.2023	ARSR Green 930

***All inks used were procured from M/S. Sakata Inx (India) Private Limited**

3.15. Fabrication of the LD /LLDPE Co-extruded Laminated films

Unsupported printed films like printed LD /LLDPE co-extruded films are commonly used for packing non critical fast consumed items requiring not so much stringent barrier properties and short shelf life. Mostly the milk pouches and packages for fast foods having little affinity towards water vapor belong to this category. In such cases the printing is carried out on the treated surface of the film and the other surface (untreated one) goes for the sealing purpose once the contents are packed. However, in majority of the cases, particularly for sensitive products it is almost always necessary to juxtapose or laminate another barrier film to the soft flexible LD/LLDPE co-extruded film which goes not only to improve the barrier characteristic of the ultimate combination remarkably but also imparts high mechanical properties like stiffness, rigidity, puncture resistance and other attributes which were impossible to conjecture to achieve with a unsupported flexible film. In the packaging industries mostly Polyester (PET) and Biaxially Oriented Polypropylene (BOPP) films are recommended exclusively for this purpose. In such specification, PET or BOPP is first printed as per the design in the gravure printing machine. It is followed by the process of lamination in which the printed surface is coated with solvent laden adhesive and the coated surface is thoroughly dried by allowing it to pass through the drying tunnel. Once it emerges from the tunnel end, the corona treated surface of the LDPE/LLDPE co-extruded film is immediately nipped over the adhesive coated surface and the entire combination is allowed to be stored to achieve the optimum strength. The basic objective of this investigation was to check the influences of treatment and ink on the peel bond strength of the laminate.

3.16. Study of Peel Bond Strength of PET Films Coated with Different Coloured Inks and Treated Transparent LD/LLDPE Films

In the work under discussion, the conventional industrial practice had been followed. Accordingly 12µm Polyester film having a treatment level of 41 dynes/cm had been printed with (overall lacquered) different coloured printing inks, namely yellow (coating weight 0,925g/m^2), magenta (coating weight 1.13 g/m$^{2)}$, cyan (coating weight 1.25 g/m^2), and green (coating weight 1.13 g/m^2) respectively and each coloured film was then dry laminated as mentioned above with 75µm LD/ LLDPE Transparent co-extruded film having surface tensions of 36 dynes / cm (3.0 kW), 38 dynes/cm (3.5 kW), 40 dynes / cm (4.0 kW) and 42 dynes /cm (4.5 kW) respectively. The details of the type of adhesive applied for lamination (over the coloured surface) are being given below in Table-3.6.

Table-3.6: Conventional Commercial Films/Substrates with the Treatment Levels on Both Sides.

Type of Adhesive	Two component solvent based polyeurathane
Binder	Brilliant G 180 Solids content 75%
Hardener	Brilliant W 75 Solids content 100 %
Mixing Ratio	100: 15 (Binder : Hardener)
Coating weight	2.5 g/m^2

The laminates were made from Polyester and LD/LLDPE co-extruded films with the bonding agent as detailed above subjected to two main technical testing for evaluating the performance of the laminates. The treatment levels on the surface of the films undergoing corona treatment at different wattages have already been mentioned in our earlier discussion. The two tests namely peel bond strength and the corresponding heat seal joint strength were determined as per ASTM D 903 and ASTM F 88 respectively **[20,10].**

3.17. Study of Peel Bond Strength of a Laminate Composed of Reverse Printed 12 µm PET Films (coloured side being laminated) and the 75 µm Treated Co-extruded LD/LLDPE Opaque White Films

In a previous work (ref. Section 4.2) **[22]** the behaviour of opaque white LD/LLDPE film surface on corona treatment at different applied voltages was studied exhaustively. In the present work the lamination behaviour of this film treated at a specified kW was studied, In doing so 12 µm PET film was lacquered overall with inks as mentioned under section 4.1 and the coloured surface was laminated to 75 µm treated co-extruded LD/LLDPE opaque white film being treated at 4.5 kW. The adhesive used was the same as given earlier and the adhesive coating was 3.0 g/m^2 (GSM) identical to our previous work on lamination (ref. Section 4.1). The surface treatment levels for the PET film and the LD/LLDPE films were 41 dynes/cm and 36 dynes/cm respectively. After optimum curing of 48 hours at room temperature these laminates were subjected to peel bond strength as per ASTM D 903 **[19**].

3.18. A Comparative Study of the Peel Bond Strength and Heat Seal Joint Strength of the Laminates Comprising of Conventional Commercially Treated Polyester and BOPP Films with Treated LD/LLDPE Co-extruded Films

In order to ascertain the influence of ink film on the peel bond strength and consequently the heat seal joint strength of conventional treated films available in the market (over which printing ink was laid down followed by its lamination with stretchable treated LDPE films) were collected and dry laminated with 75 µm co-extruded LD/LLDPE films being treated at 4.0 kW using the same bonding agent as was used earlier under identical conditions of lamination (coating weight of solid deposit of adhesive, nipping pressure, drying conditions, maturing time etc.) **[23].** In this experiment, different transparent substrates as mentioned below were used straight way without being inked or lacquered. All the laminates of PET/adhesive /LD-LLDPE film and BOPP/adhesive/ LD-LLDPE film were subjected to sealing under similar pressure and dwell time of 7 sec. The sealed samples were cut into strips of 1 inch width. The heat seal joint strength was determined as per ASTM F 88 **[10]** in the Universal Testing Machine with a load cell of 1000 N and jaw speed 300 mm/min.

3.19. Scope and Objective of the Present Work

From the literature survey it can be readily envisaged that there is ample scope of investigation on the utilities of “CORONA TREATMENT” particularly where lies the problem of surface adhesion. It is needless to say that the majority of plastic films normally dealt in flexible packaging industries have surface problems like poor spread ability and poor wettability that lead not only to lack in adhesion but also poses a great threat in having a proper acceptable surface finish. In this age of multilayered packaging materials the problem has become much more aggravated because of varying chemical compositions of the films having a wide variety of surface energies and topography. Till date there is no established document regarding the range of surface energy /surface tension that can be achieved from corona treatment at different applied voltages. A scientific correlation between the applied voltage (Load) and the level of treatment (surface tension) achieved is really lacking. Most of the relevant industries operate on “Hit and miss” policy. We are still in the dark about what should be the optimum surface energy on the different non polar, semi-polar or polar films that could offer good printability and adhesion characteristic acceptable to the packaging industries. Although this is an arduous task to prepare a comprehensive and concise data for this but its necessity cannot be over emphasized. We can find from the survey that there is no report on whether it would be prudent to carry out the process of treatment in situ during the fabrication (extrusion) of the film or it would be beneficial to do the same at a later stage. This is an imminent problem in industries dealing in corona treatment as sometimes they do not have either the infrastructure of doing so or they are pre occupied with the idea that an in line corona treatment during processing of the film at a later stage may be much more beneficial. There is no detailed report on such ambiguous issues.

Sometimes in secondary operations the corona treated film remains stored in big spool forms in the warehouse having uncontrolled ambience for a prolonged period of time. No information is still available that can guide as to the fate of surface tension due to ageing in such conditions where thousands of layers of film remain in tight condition under the pressure of the layers lying above (a treated surface being in intimate contact with an untreated surface). There is also no specification regarding the time limit of such storage maintaining the charges developed initially. Whether there is any scope of charge decay or dissipation or any possibility of diffusion to the opposite surface (considered to be free of charge although there remains relatively less charge always). Once the optimum level of treatment is obtained on the plastic film surface at a suitable applied load (voltage) sufficient for having good printability with a proper adhesion it is quite pertinent to study the effect of applying overload so as to develop surface tension more than optimum. A knowledge of the deleterious effects (if any) of such overtreatment would definitely ensure in maintaining quality. Besides, an overtreatment would lead to incur added cost.

Sometimes it becomes necessary to incorporate various additives namely, colorants (Pigments), process aids, thermal stabilizers, antistatic agents, slip additives, antioxidants, blowing agents, etc into the film in order to cater to various specific needs as demanded by the end use. It has nowhere been studied, the influence of such additives on the development of surface charges during the corona treatment. Secondly, it is also not known how these additives would behave with the surface polar groups developed during corona treatment. There is no concrete information on the doses of such additives that would not stand in the way of development of optimum surface energy. The physical and chemical nature of the additives, its dipole are still awaiting and thus offer space for further investigation.In making a suitable packaging specification, it can be observed that a particular web (a film, may be

PE, PP, PET, PVC etc.) has to undergo a number of processing. A particular surface of the film goes on getting renewed in several steps. Thus in case of a simple PET / PE laminate, the operation starts with PET film of certain thickness and a specific surface energy. Once printing is done on a surface, it gets a renewed surface where the printing ink provides a continuous or a discontinuous ink surface. As lamination of the second surface is designed on this new surface, adhesive is coated on the inked surface. Now the surface energy of the ink surface plays dominant role in proper spreading and wetting of the particular adhesive. Now, the ink has definitely a specific surface tension. On getting spread on a treated surface, can the ink maintain its own surface energy or a new surface energy develops due to the physical interlocking of the ink surface and the original PET surface. There has been no such study as such in the literature. This results in frequent delamination, poor lamination and no lamination at all. A thorough study is still lacking.

Thus it can be observed that there is a myriad of dark areas concerning surface treatment by corona method. Half information or no information in this field of technology are supposed to create innumerable problems, the scientific solutions of which are not yet available. The present dissertation has been prepared to address a few of these challenges. Attempts have been made to find answers to the following problems.

1. A correlation has been sought between the applied electrical load (kW) and the resulting surface energy / surface tension developed on films composed of LDPE-LLDPE blend, the most extensively used one in packaging industries both as a monolayer and in multilayer specifications.
2. The optimum load, i.e. where the maximum surface energy is achieved and beyond which further increase in load does not lead to any further significant enhancement in surface energy does not occur has to be evaluated so that a guideline can be made for industries dealing in such treatment processes.
3. Conventional Dyne solution (made of Ethyl cellosolve and Formamide mixed in different proportions to achieve different surface energy levels) has been used for quick evaluation of the surface energy developed during commercial production of corona treated LD-LLDPE film. The solutions with different surface energies have been standardized and compared to the values of equilibrium contact angle as obtained from Goniometer on the same surface of the film.

An approximate relationship between the contact angle and the surface energy of the dyne solution on the same film surface has been elucidated.

4. The present work is also initiated to resolve the most acute industrial problem arising out of dearth of information on the optimum level of treatment that can lead to hassle free operations to be followed for fabrication of a film destined for packaging application.
5. The different surface properties of the film (LD-LLDPE) both physical and chemical are supposed to be greatly affected by virtue of this corona treatment The course of changes in such properties including its topography are quite critical in determining the behavior of the subject film during its subsequent processing. The study of these properties is thus very important and needs meticulous investigation as has been proposed in the present work.
6. It has been attempted to study changes (if any) in the mechanical properties of the film due to corona treatment. A plausible explanation regarding the results of such investigation has been sought.
7. The possible influences of the presence of suitable pigment (Titanium dioxide, TiO_2 in the present work)on the performance of the corona treatment process have been attempted to be investigated. Whether the level of treatment achieved with such opaque pigmented film matches the same on a transparent film of same thickness and composition under identical conditions of treatment is investigated and the observations are noted. Any possible deviation is explained.
8. Starting with such treated film when some secondary operation like printing or coating etc. is done on the treated surface, the ultimate treatment level or the surface tension on the coating is measured and corroborated with the surface tension of the coating medium and the initial treatment on the original substrate itself. This might be quite helpful particularly when the coated film is supposed to undergo a further processing on it. The selection of the appropriate coating or laminating material would be easier and faster in such cases. This is being proposed not only for the LD-LLDPE film fabricated at the author's end but also for several other films like, PP, PVC, PET, PET-G, MET-PET etc.
9. Finally a comparative study is being proposed to be made.

10. The role of surface energy /tension prevailing on the surfaces of different flexible films mostly used in packaging industries cannot be over-estimated. The level of Corona treatment available on different film surfaces endows it to behave differently to various coating materials. There are no stipulations in respect of necessary surface energies' levels on the different films and no guidelines for specified coating media.

A proper guideline would be sought in this regard.

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Chapter 4:

RESULTS AND DISCUSSIONS

4. RESULTS AND DISCUSSIONS

This section embodies systematic collection of all the experimental results of the present research work. The plausible explanations of such results and the correlations amongst them have been sought scientifically and possible attempts have been made to corroborate the results with earlier findings (if any). Exceptional results have been mentioned specifically and the causes thereto have been discussed critically.

4.1. Effects of Corona Treatment on Surface Properties of Co-extruded Transparent LD/LLDPE film

Natural co-extruded LD/LLDPE films consisting of three layers, (the composition of each layer being elaborated under experimental section) were fabricated in the co-extruder. The films were 75 µm in thickness and the overall thickness was shared equally in the three layered structure. The films were subjected to corona treatment in tandem with its fabrication (the flattened bubble being treated on its outer surface followed by slitting at the edges into two equal halves and tightly wound on spools at a definite haul-off speed). The treatment side was always by default the outer side of the spool. Different samples spools were hence produced at different treatment levels by applying different kW at the corona treater unit.

4.1.1. Effects of Voltage on Surface Energy of Transparent Film

Figure-4.1 shows the surface energy (treatment levels) achieved with the variations in applied voltage (wattage). The wetting tension (surface energy) or the extent of treatment level on the surface of a transparent LD/LLDPE film steadily increased with the increase in wattage (Load) applied in the corona discharge unit. The nascent O_3 which was formed in the treater unit during discharge was a powerful oxidizing agent. This O_3 along with other ionizing particles were associated with very high energies in the order of 10–20 eV. **[1]** The particle energy being a function of the applied voltage, the particles were more and more energized with the increase in voltage or the wattage applied. In the present study, the treater unit was capable of generating a maximum wattage of 5.0 kW and hence studies had been restricted up to a maximum of 4.5 kW. The increases in energies of the various particles discharged in the corona treater enabled it to bombard on the film surface both at a faster rate and in greater numbers steadily as the applied load was increased.

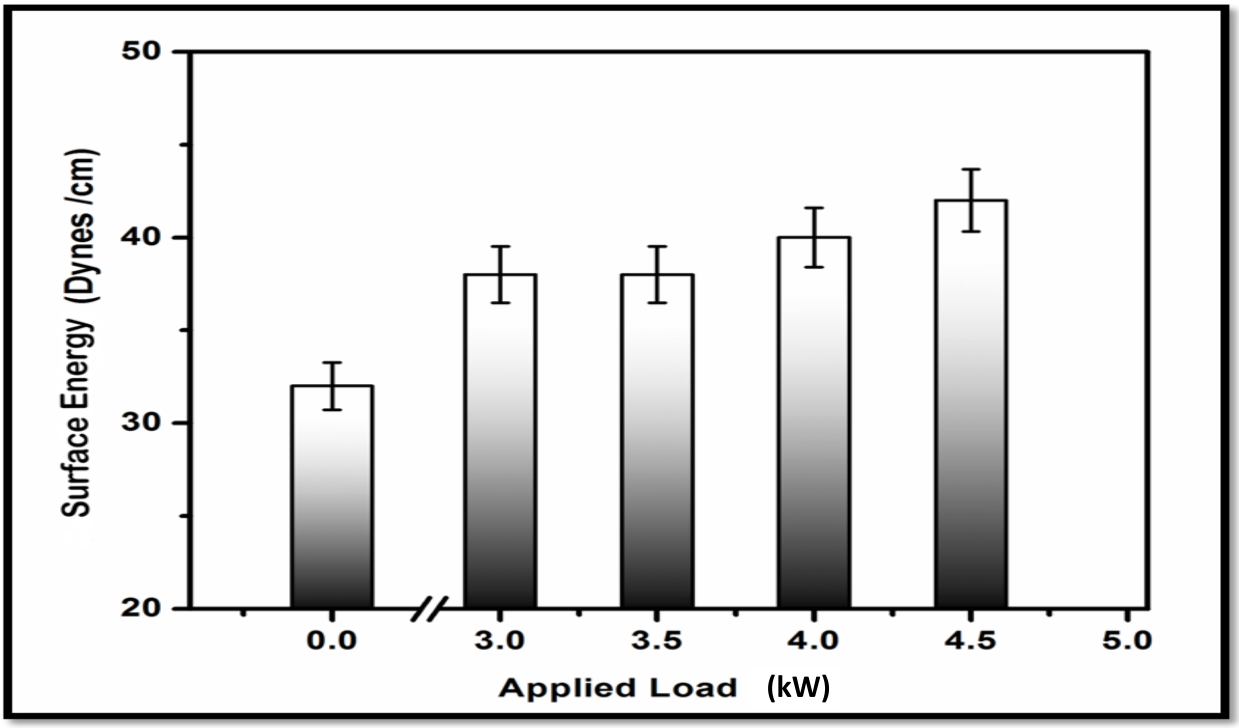


Fig-4.1: Surface energy versus applied load for a 75 µm transparent linear low density polyethylene/low density polyethylene (LLDPE/LDPE) film

The treatment level increased with increase in voltage applied for discharge. It was observed that a wetting tension of 34 dynes/cm (as measured by the dyne solution technique) or above was generally required for printing, while still higher levels greater than or equal to 42 dynes/cm were necessary for lamination or extrusion coating application. It can be readily observed from figure-4.1 that compared to the untreated film (where the applied voltage was zero), there was an immediate jump in surface polarity even at the lowest wattage applied (3.0 kW) at the Treater. Although there was a progressive increase in treatment level with the increases in applied wattages, the correlation between the power consumption and the level of surface energy achieved was not linear and this non-linearity was further affected greatly by the level of slip additive present (if any). The enhancement in surface polarity was, however, slow and not so much pronounced as was being expected particularly at the higher voltages applied within the range under study. It can possibly be argued that at higher wattage, although the generation of energized active species, that was ions, electrons, radicals, and so forth, got enhanced, a substantial fraction of these were annihilated due to interactions among themselves before any interactions with the active sites of polyethylene surface occur.

The changes which occur mainly on account of bombardment of electrons, ions and neutrals affect the material only over a range of hundred to several thousand angstroms in depth. For polymeric substrates, the main effects are in terms of etching (loss of molecular weight), crosslinking, oxidation and other chemical properties of polymers such as permeability, solubility, melting point and roughness at the surface **[2]**.

It would be quite pertinent to mention here that the commercial film used in this investigation contained slip additive on the surface away from the surface getting treatment. However, the influences of slip additive might be expected to vary depending on its state of existence in a multilayered co-extruded film, that is, whether it was present in the layer to be treated itself or it was in the farthest layer. In order to find out the influence of slip additive, a polymeric film of identical composition and thickness but without any slip additive in any of the layers was fabricated in the same extruder under identical conditions of process parameter, the only exception was the load applied at the treatment unit, which was maintained at 4.5 kW. It was observed that a treatment level as high as 56 dynes/cm was achieved in the desired layer.

4.1.2. Effect of Surface Energy on Peel Adhesion Force of 3M Scotch Tape Adhered on Transparent Film

The higher the surface energy, the higher was the level of peel adhesion forces of a standard adhesive tape as shown in figure-4.2. The tensile load required to separate two smooth bodies remaining in close contact is known as the Pull Off force which is related to the thermodynamic work of adhesion by the Jhonson, Kendall, and Robert (JKR) theory. The basis for JKR theory was the mechanical equilibrium between the energy released due to adhesion and the elastic energy stored due to the deformation of the contact zone **[3].** The forces of adhesion of a standard scotch tape on an untreated surface of the transparent film were considered as those obtained from peel adhesion force on treated surfaces of the transparent films under study. This was in corroboration with the findings as explained above and verified the scope of increasing adhesion with increases in applied voltages. The variation of forces of adhesion or peel strength (i.e. the force required to peel the tape from the surface of the film over a specified width of the tape) was measured in a Tinus Olsen make Universal Tensile Testing Machine and was shown in figure-4.2.

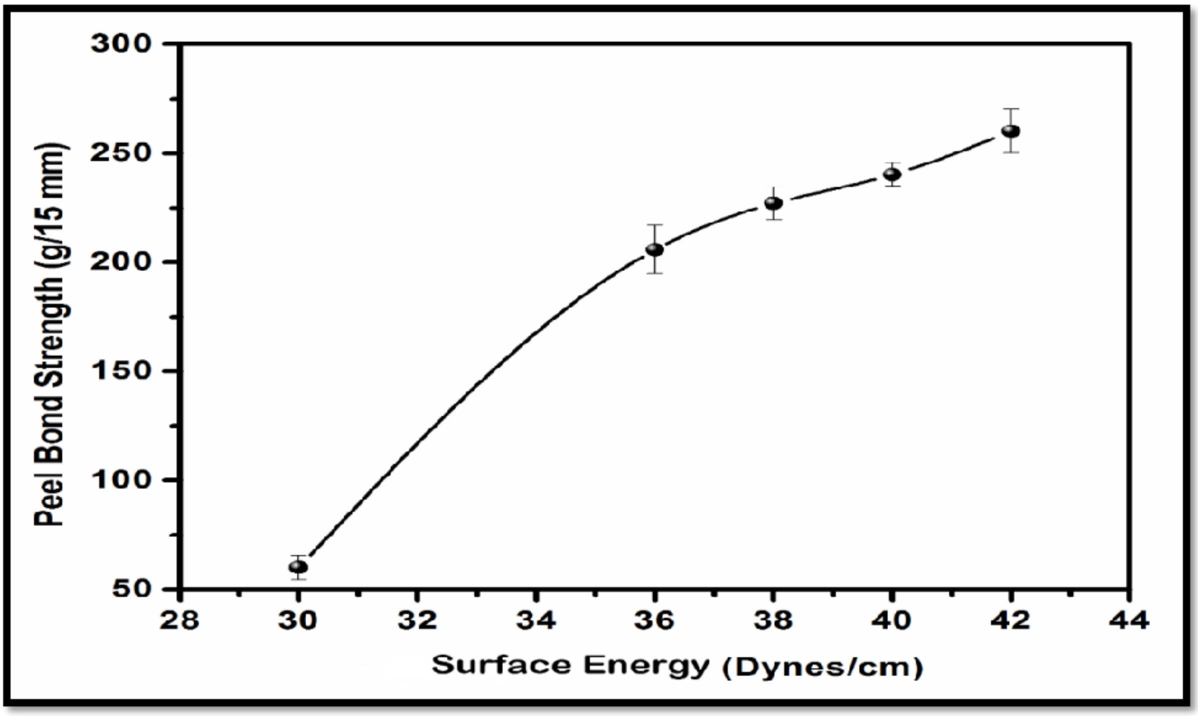


Fig-4.2: Surface Energy vs Peel Bond Strength for a 75µm LLDPE/LDPE Transparent Film

It was observed that the peel adhesion increases with increase in level of treatment, that is, with increase in wattage (voltage) applied. The untreated surface highlighted a treatment level of 30 dynes/cm, which was assumed to be generated on the inside of the bubble during its fabrication at the extruder. The surface molecules on the outside of the bubble which were exposed to the bombardment of high energy particles (corona discharge) were subjected to undergo transient dipole changes within themselves under its influence leading to the enhancement in overall dipole moment of the film and hence in surface energy. Following the trend observed in our earlier experiment, a remarkable increase in peel adhesion was observed when the force of adhesion on the treated surface was compared to that obtained on an untreated surface even at the lowest wattage applied within the range of studies. At higher levels of wattages applied, however, although there was a steady increase in peel adhesion, the effect was not so much pronounced. This can be attributed to the effective concentration of active energetic particles available for interaction with the surface, which appears to reach an equilibrium value at higher wattages as explained in the previous section. It was expected that corona treatment of polymeric surfaces create wettable polar surfaces on which the adhesive of the tape may spread spontaneously and hence, provide extensive interfacial contact between the tape and the treated film under investigation. It is known that extensive interfacial contact is a necessity for good bonding, but not a sufficient condition for forming strong joints. The primary function of surface oxidation techniques is to remove the weak boundary layer. In fact, if surface oxidation alone would have occurred without removal of a weak boundary layer, only weak adhesive joints would be obtained **[4].**

4.1.3. Fourier Transform Infrared (FTIR) Studies of Transparent Film

The FTIR absorbance spectra of 75 μm transparent coextruded film sample consisting of 10 layers as suggested by a group of researchers [**5,6]** in order to have a measurable effect of treatment made from LDPE/LLDPE blend (the same blend was used in all the three layers) are shown in figure-4.3. It is worth mentioning here that the treated surface was used as the reflectance surface while taking the spectra in an ATR mode. For the sake of comparison, the spectrum of an untreated film was also considered. The peak at 2915 cm^{-1} stands for unsymmetrical stretching in methylene (-CH_2-) group and the absorbance peak at 2847 cm^{-1} was attributed to the symmetrical stretching in methylene group. The peak at 1463 cm^{-1} was accountable for deformation of methylene groups perpendicular to the chain axis. The small hump at 1368 cm^{-1} also stands for the deformation of methylene groups.

The doublet at 720–730 cm^{-1} was characteristic of solid polyethylene and crystalline paraffin hydrocarbon. The absorption band at 720 cm^{-1} was assigned to the rocking of the hydrogen atoms in the methylene group. Splitting of the single absorption band at 720 cm^{-1} into a doublet absorbing at 720 and 730 cm^{-1} occurred on crystallization because of the interaction of the methylene groups in the crystalline regions. The development of some new peaks in the FTIR spectra of treated films might possibly be leading to indicate some chemical modification on the exposed surface. The evolution of some oxygen containing functional groups although not so sharp and prominent on the surfaces of films treated at different applied voltages appeared to confirm surface oxidation and hence the chemical modification due to corona treatment.

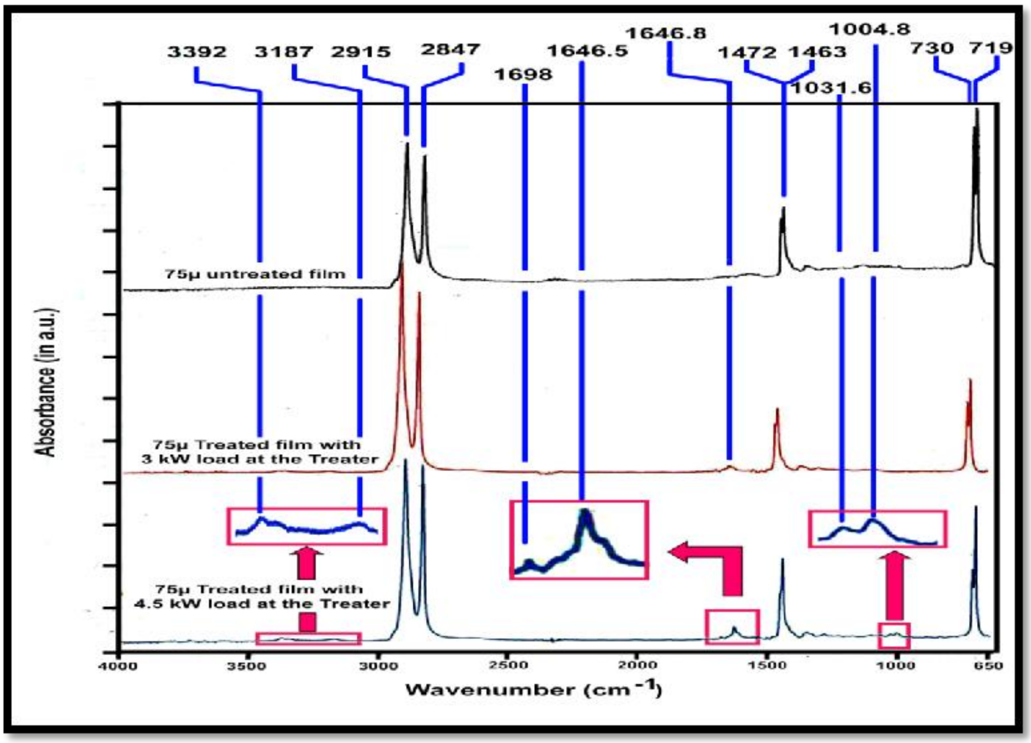


Fig-4.3: FTIR absorbance Spectra for the 75µm Untreated and Treated film with 4.5 kW and 3.0 kW Loads.

The small hump in the region of 3200 cm^{-1} for the two treated samples under consideration corresponded to hydroxyl (-OH) groups. These were, however, absent in the untreated sample. The presence of carbonyl group (C=O) was indicated by the peak at 1646 cm^{-1}. It appeared due to axial deformation of C=O group which was formed due to corona treatment. Similar observations were also reported by Louzi et al.**[7]** The peak corresponding to C=O stretching was also found to appear at 1031.6 cm^{-1}. It is important to mention here that the film under investigation in the present work was a transparent one and consists of three layers out of which one layer contains slip additive. This slip additive (EURACAMIDE) was an amide type of compound which was supposed to exhibit IR peaks corresponding to both C=O and NH_2 groups. In case of the present work, the carbonyl peak C=O of the slip additive (amide) was also supposed to appear in the same region as that had been observed for the newly generated carbonyl group due to oxidation on corona treatment, that is, at 1646 cm^{-1}. Hence, in the case of the treated film, both these carbonyl and amine peaks have possibly superimposed on each other so as to make them indistinguishable. However, on deconvolution, a small peak (hump) at 1698 cm^{-1} appeared only in case of the treated films and this might be attributed to the C=O generated due to oxidation during corona treatment. A much weaker ester group (O=C-O-C) was also present as a very minute band at 1166 cm^{-1} in the spectra **[8-11]**. A small hump at 1038 cm^{-1} was attributed to the formation of olefinic unsaturation which preludes to the process of oxidation. It would be quite pertinent to mention here that in a review paper by Sun Christine et al.,[**8**] it had been mentioned that the surface oxygen elemental concentration in a typical industrial process of corona treatment varied from 10 to 18% depending on the energy density level and the consequent introduction of polar groups on the film surface in the form of carbonyl, carboxyl, and so forth, groups leading to surface energy in the range of 33–55 dynes/cm. This was confirmed by X-ray photoelectron spectroscopy analysis.

4.1.4. Effect of Voltage on the Heat Sealing Characteristics of Transparent Film

In flexible packaging, LDPE and LLDPE in isolation or in their blended form in suitable proportions is usually present as the inside sealing layer and this plays a pivotal role in providing an integrated sealing to the pouch or the sachet so as to give proper barrier to the packaged item. The seal is supposed to be leak proof, pilfer proof and resistant to toxicants and impermeable to all environmental gases. With the advent of different designs in packaging, it has sometimes become imperative to carry out this sealing process with different combinations of treated and untreated surfaces. The basic objective of this study was to investigate how these different combinations, namely untreated/untreated, treated/untreated and treated/treated surfaces affect the heat seal joint strength of the sealed bond. Individual set of studies had been undertaken with each level of treatment obtained at different power loading or wattages. Figure-4.4 gives a document of heat seal joint strength for the three different combinations of surfaces as mentioned above, achieved at wattages of 3.0; 3.5; 4.0, and 4.5 kW, respectively. From the bar diagram, it could be readily observed that the heat seal joint strength for the untreated/untreated surface combination (U-U surface) almost remained the same irrespective of voltages applied for corona treatment on the opposite sides of the said film combination. It might hence, be concluded that the heat seal joint strength for the combination of untreated/untreated surfaces was independent of the extent of treatment level on the opposite sides or the charge on one side had little influence on the heat seal characteristic of the other (untreated) side. Hence, the corona treated polyethylene films were considered to have macroscopic charged bilayers **[12].** The constancy of the heat seal joint strength for the other two combinations of sealing surfaces (i.e., untreated/treated (U-T) and treated/treated (T-T)) within the range of applied wattages under study also followed the same pattern as that exhibited by the untreated/untreated combination. However, the values of heat seal joint strength undergone remarkable decrease compared to the untreated/ untreated combination at the corresponding voltages considered. The order of decrease in heat seal joint strength was shown as untreated/untreated > untreated/treated > treated/treated surfaces. The observed changes in figure-4.4 particularly for the untreated/treated and treated/treated surface combinations might be attributed to the surface roughness initiated by treatment on the treated surface. Furthermore plausible crosslinking of the surface molecules initiated by treatment was supposed to intensify the problem of perfect sealing. Hence, the treated surface was oxidized and cross-linked as well leading to reduced polymer mobility and an enhancement in melting range **[13].** For comparison purpose all parameters of sealing i.e. sealing temperature, sealing pressure and dwell time was kept the same, a situation was reached where an heterogeneous combination of melting surfaces was obtained leading to improper peel-able sealing for the untreated/treated combination of surfaces.

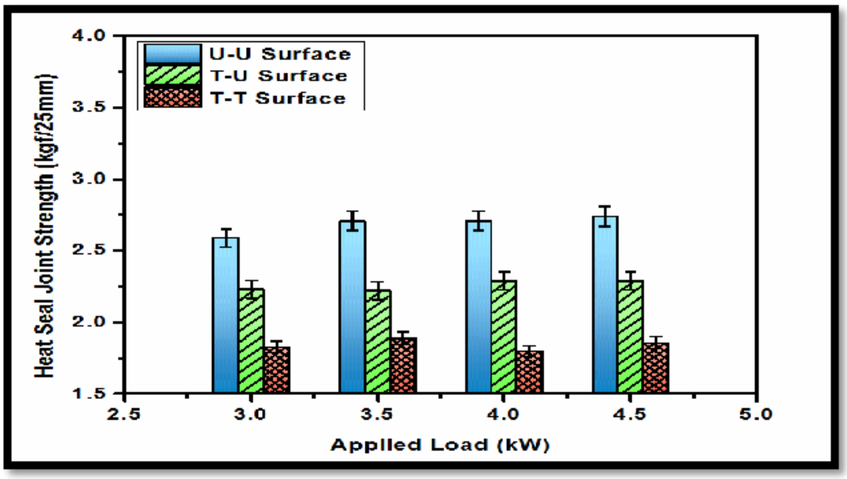


Fig-4.4: Characteristics of Heat Seal Joint Strength of the 75µm LDPE/LLDPE transparent film at different surface combinations.

In the third combination of treated/treated surfaces, the condition became more stringent and both surfaces being oxidized and cross linked were quite resistant to melting and thus, provided the lowest heat seal joint strength. In almost all packaging industries, the equipment designated for forming pouch/sachet, and finally for sealing the packed contents is set to run at a given temperature and at a given speed such that sufficient dwell time is ensured for proper sealing. In fact, the sealing temperature, dwell time of sealing, and sealing bar pressure had all been set as per the specifications of the concerned industries. The corresponding observations had been represented in the form of bar diagram in figure-4.4. The main objective was to determine the actual seal strength achieved and it could be ensured that the observations were almost coincided with those of the concerned industries. Secondly, it was evident from the common experience over years that a treated side of a film on sealing with either an untreated or treated side of another film always yielded very poor seal strength after sealing under identical conditions of sealing an untreated/untreated combination of surfaces. The problem became most crucial for treated/treated surface combination. It was the oxidation of the surface due to treatment that raised the melting range. If the temperature was raised to that level or the sealing time was increased there was every possibility that the contents within the pack might undergo thermal degradation because of the enhanced heat flux in the sealing region.

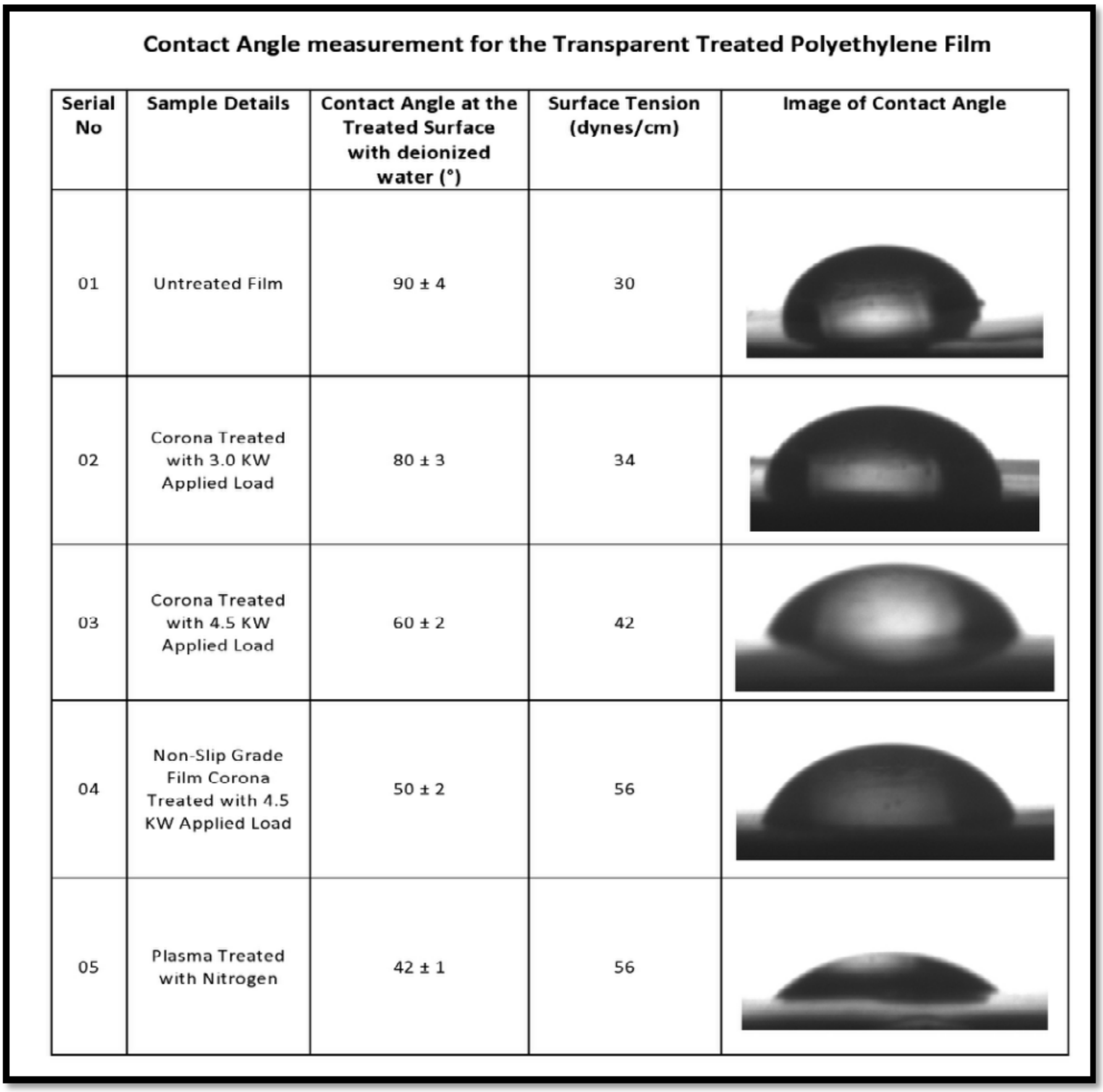
4.1.5. Effect of Voltage on the Contact Angle of Transparent Films

Wetting and spreading characteristics were considered to be the most important parameters in packaging industries as the different types of adhesives, coatings, and printing inks used in such sectors were supposed to spread on the film under consideration. The contact angle was measured on the treated side of the LD/LLDPE film by observing the equilibrium angles formed by the conventional sessile fluid on its surface.

In this connection, a comparative study had been made to investigate the mode of changes in equilibrium contact angle made by a drop of de-ionized water on the surface of an untreated film of identical thickness vis a vis the equilibrium contact angles achieved on the surfaces of films which were treated at different wattages and the consequent surface tension obtained by applying standard wetting solutions. The contact angle (C.A.) (θ) was measured by the sessile drop method. The height (h) and radius (r) of the spherical segment formed by a small drop of double distilled deionized water dropped on the surface were calculated and the angle was obtained by equation:

$$\boldsymbol{\Theta = \mathrm{Sin}^{-1}\,[2rh/\,(r^2 + h^2)]} \qquad \textbf{[14]}$$

The equilibrium contact angle formed on film surfaces treated at different wattages was presented in figure-4.5.



Contact Angle measurement for the Transparent Treated Polyethylene Film

Serial No	Sample Details	Contact Angle at the Treated Surface with deionized water (°)	Surface Tension (dynes/cm)	Image of Contact Angle
01	Untreated Film	90 ± 4	30	
02	Corona Treated with 3.0 KW Applied Load	80 ± 3	34	
03	Corona Treated with 4.5 KW Applied Load	60 ± 2	42	
04	Non-Slip Grade Film Corona Treated with 4.5 KW Applied Load	50 ± 2	56	
05	Plasma Treated with Nitrogen	42 ± 1	56	

Fig-4.5: Equilibrium Contact Angle vs. Applied Wattage in the treatment unit

An untreated film of identical thickness was fabricated under identical conditions in the same extruder and was subjected to plasma treatment off–line in an atmospheric pressure plasma treater. The equilibrium contact angle of deionized water film on such plasma treated film was measured and reported. It could readily be perceived that the contact angle gradually decreased with increase in wattage and hence, corroborated the earlier findings. The wetting by deionized water film was observed to be maximum with the plasma treated film. However, this method of surface modification was very effective one. Unfortunately, the plasma treatment is yet to find extensive usage in industries as it is indeed a capital intensive and a moderately slow process. Pascual et al.**[15]** in a similar type of study made identical observations as the polar component of the surface energy underwent significant increases from very low values of 2.6 mJ/m^2 for untreated LDPE film samples up to value near 19 mJ/m^2. In the work of Pascual et al., the surface energy was determined by a Goniometer (a lab equipment) using different sessile fluids of known “Dispersive” (γ_D) and “Polar” (γ_P) surface energy components and the contact angle of these liquids used to develop on the surface of the film. The individual surface energy components as mentioned above for the treated film surface was then calculated from the plot of (γ_{lP}) 0.5 (γ_{lD}) 0.5 versus γ_l (1+ cosθ)/2 (γ_{lD})0.5 following the Owens–Wendt method **[3]** where γ_{lP} and γ_{lD} are the polar and dispersive components of the surface energy of the liquid and θ was the equilibrium contact angle formed by the liquid on the surface of the film. From the slope of the line in the plot, the polar component and from the intercept on the Y axis, the dispersive component of the overall surface energy of the film was calculated. The sum of these two components ultimately stood for the surface energy of the subjected film. Fowkers equation **[16]** which resembled Owens-Wendt method can be used for this purpose. It had been observed that the dispersive contribution (untreated surface) remained almost always constant near a value of 26 mJ/m^2 or 26 dynes/cm, while the polar component of the film after treatment underwent an increase from 2 mJ/m^2 (dynes/cm) to 19 mJ/m^2. Thus, the total surface energy achieved by Pascual et. al was, (26 + 19) = 45 mJ/m^2. However, this is a tedious and a time-consuming process for commercial production. In our case we could find that the dispersive component was approximately 30 dynes/cm (i.e. on the untreated film surface), whereas on treatment, it reaches to 42 dynes/cm. Thus, the present method describes a very quick process of surface energy determination which approximates the theoretical value. In the present work, the objective was to determine the level of surface treatment that was sufficient for subsequent coating, lamination, printing, etc. processes on the shop floor and to find out the individual surface energy components. Thus, the shop floor method could be considered an authentic one providing reliable values and guiding parameters.

4.1.6. Effect of Voltage on Coefficient of Friction of Transparent Film

Case–I: Film to metal surface

A graphical representation of the mode of changes in both static and kinetic coefficient of friction while a treated surface of a film was allowed to slide over a metallic (smooth iron surface) is depicted in figure-4.6. In this case, it was observed that the static coefficients of friction remain almost unchanged up to a load of about 3.5 kW beyond which it undergone a steep and steady increase within the range of load under study. In contrast, the kinetic coefficient of friction increased with increase in applied voltage at a steady rate right from the lowest applied voltage and reached an optimum beyond which a further increase in applied voltage led to a sluggish rate of rise in kinetic coefficient of friction. Static coefficient of friction at any applied voltage was always higher than the kinetic coefficient of friction at the corresponding applied voltage. It can possibly be argued at this juncture that the increase in roughness attributed to enhanced micro-etching at higher applied voltages led to the observed increase in kinetic coefficient of friction. The static coefficient of friction, however, appeared to be insensitive towards the changes in applied voltage.

Case-II: Film to film (Surface)

The mode of changes in both static and kinetic coefficients of friction when the treated surface of a film was subjected to friction over the untreated surface of the same film is described in figure-4.6. The static coefficient of friction in this case also remained higher than the kinetic ones at all the applied voltages considered. Within the range of applied voltage under study, the static coefficient of friction undergone an increase of about 38% only while the kinetic coefficient of friction undergone an increase in the order more than 1000%. The roughness on the treated side of the film was more likely to dominate and control the kinetic coefficient of friction much more than that was observed with the static one. In a manner similar to that observed with film to metal surface, the static friction appeared to remain almost unchanged at higher applied voltages although the changes at the lower end of the applied voltages was quite significant.

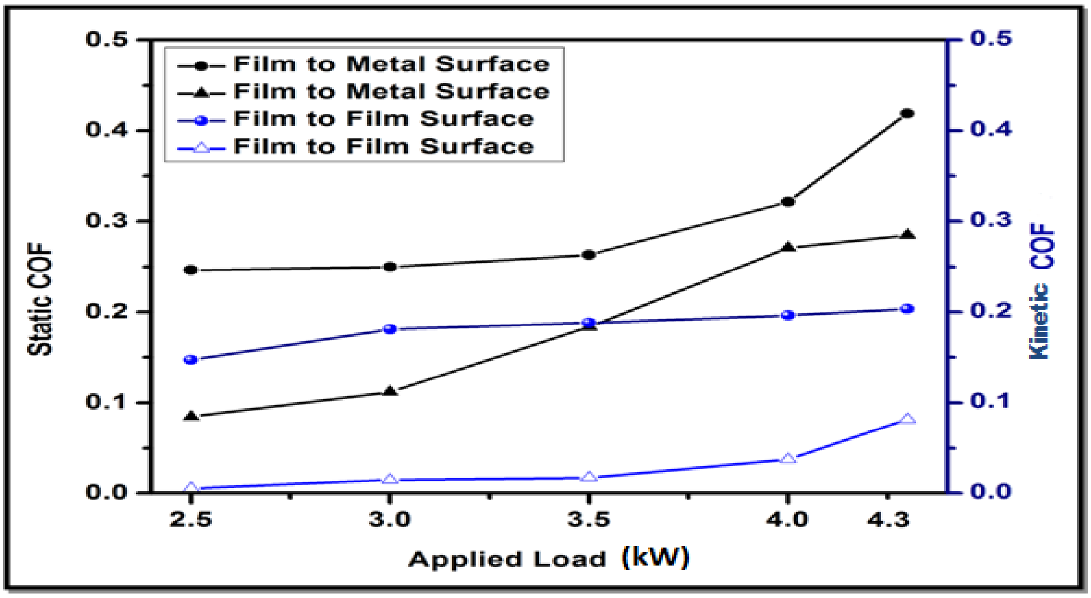


Fig-4.6: Static and kinetic co-efficient of friction for film to metal and film to film surfaces as a function of applied load.

4.1.7. Mechanical Properties of Treated Transparent Films

In order to investigate the influence of corona treatment on the mechanical properties of the co-extruded film, mechanical performances of the treated film samples were compared to those of the untreated ones. The comparative analysis was represented in Table-4.1. There were hardly any differences in any of the mechanical parameters of the treated films and the untreated ones. The mechanical properties were considered as the bulk properties while the process of corona treatment changes the physicochemical properties of the surface layer only. Hence, the mechanical properties of the film remain unchanged after treatment.

Table-4.1: Mechanical Properties of the 75µm LDPE/LLDPE Transparent Film before and after Corona Treatment on the film.

Direction	Elastic Modulus (MPa) Tested as per ASTM D 882	Yield Stress (MPa)	Peak Stress (MPa)	Break. Extn (%)	Tensile Energy Absorption (TEA) (J)	Tear Resistance (gf) as per ASTM D 1004	Impact Energy (gm) as per ASTM D 1709 before Treatment	Impact Energy (gm) as per ASTM D 1709 after Treatment
Machine Direction (MD) and BeforeTreatment	108.6	12.1	24.2	628.6	8.6	1072.3	419.5	419.0
Machine Direction (MD) and after Treatment	109.5	12.5	23.9	627.5	8.5	1073.0		
Cross Direction (CD) and Before Treatment	156.2	11.2	23.5	683.8	8.3	1236.8		
Cross Direction (CD) and after Treatment	155.8	11.5	22.9	684.0	8.4	1235.5		

4.1.8. Morphological Observation

It is believed that as a result of the corona discharge process, the long molecular chains on the polymeric film surface polarize and break into shorter polymer pieces. This breakage created micro-roughness on the surface. The tips of these small pieces were mostly oxidized to form –OH, > C=O, -COOH, epoxy, ether and ester groups, aldehydes, peroxides and so forth.

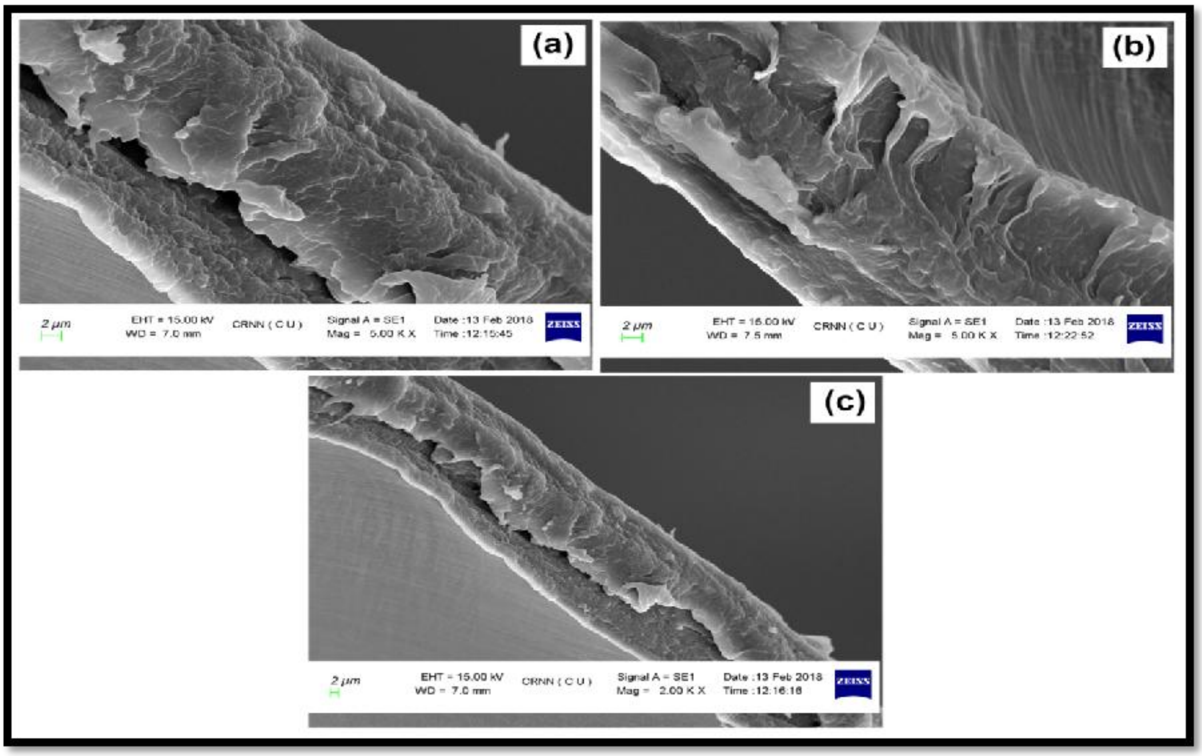


Fig-4.7: Surface Morphology of the (a) Corona Treated Surface of Transparent LD/LLDPE film with 3.0 kW Load, (b) Corona Treated Surface of LD/LLDPE with 4.0 kW Load and (c) Untreated Transparent surface of the LD/LLDPE Film.

Figure-4.7(a),(b) depict the surface morphology of the corona treated polyethylene surface at different wattages, while Figure-4.7(c) showed the same for untreated surface. Corona charging had a pronounced effect on the morphology of the film surface directly exposed to corona but had been found to have no influence on the reverse side **[12]**. In the present case, a granular and somewhat etched surface on the treated side of the film was observed to appear and this made the treated surfaces stiffer and rough. The relatively uniform texture of the untreated film was modified after treatment. Such appearance of granular surface had been reported in the literature **[17-19]** where the extent of such formation of granular surface had also been shown to be dependent on the exposure time, temperature, and gas composition during the treatment. Kim et al.**[18]** opined that characteristic of granular formation was caused by the degradation of polyethylene molecules below an inert skin since the gas evolved during the degradation process might cause the top most skin to blister formation. However, Overney et al.**[20]** suggested occurrence of droplets, considering the local surface melting of degraded products formed during corona treatment. It could be seen from the present topographs that on increasing the applied load from 3.0 to 4.0 kW, the density of the granules formed on the surface undergone a remarkable increase. The formation of such rough surfaces on the treated film led to an increase in coefficient of friction which was reflected in our previous studies on coefficient of friction as a function of applied load.

4.1.9. Effect of Surface Energy on the Barrier Properties of the Transparent Film

The WVTR (water vapour transmission rate) of the film was tested in two different ways as:

(i) the treated surface of the transparent film was exposed to water vapour and

(ii) the untreated surface of the transparent film was exposed to the water vapour

Corona treatment within a specified range of applied voltages in an oxygen atmosphere on an LD/ LLDPE blended film led to surface modification when treated with 4.5 kW applied load. In the first case, the average result of WVTR was found to be 3.29 g/m^2/day and in the latter case, it was observed to be 3.32 g/m^2/day. From these results, it can be assumed that corona treatment had marginal or very little influence on the WVTR characteristic of the film. Figure-4.8 shows the result of the WVTR tested for 75 μm LD/LLDPE film when water vapour was exposed to the treated and untreated surfaces when treated with 4.5 kW of applied load. Similarly oxygen transmission rate (OTR) was tested by the equipment - Gas and Steam Permeability Tester in two different fashion i.e. oxygen exposed to the treated surface and oxygen exposed to the untreated surface. The test was conducted in the same fashion as per the specification given in the following Table-4.2 for the same specified film. The OTR values were observed 1318.30 and 1329.95 cc/m^2/day respectively. Here, also the marginal difference indicated that there no influence of surface treatment on the OTR characteristic of the film.

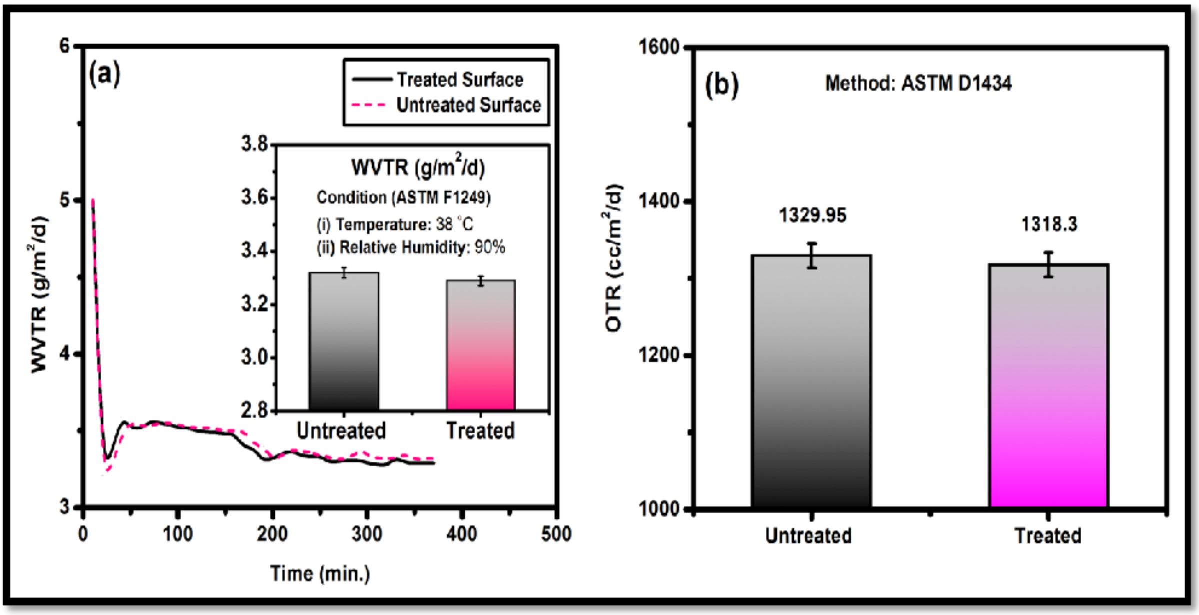


Fig-4.8: WVTR and OTR of the 75µm Transparent Co-extruded LD / LLDPE Film.

Table-4.2: OTR of 75 µm Transparent LDPE/LLDPE Film:

Parameter	Symbol		Value	Units
Sample Temperature	T	.	25	^oC
Initial height of Mercury	h_0	.	59.02	mm
Final height of mercury	h	.	7.07	mm
Thickness of Sample	T_h	.	75	Micro meter
Downside Pressure (Vacuum)	P_d	.	0.15	mmHg
Result	1318.30 cc / (m^2 x day x atm)			

4.1.10. Effect of Aging on of Surface Energy of the Transparent Film

Ageing is a process causing structural and chemical composition changes in the material, leading to the change in the functional properties of the material. The changes are mainly observed as a deterioration of functional properties. Plastic films like LD/LLDPE exposed to thermal initiation become brittle due to free radicals attacking the polymer chain followed by alkyl radicals reacting with oxygen and leading to a build up of vinyl groups and a variety of oxygen containing groups such as carbonyl functional groups **[21].**

Detailed descriptions of changes in properties and microstructure of polymeric materials were presented in literature. In order to observe the effect of aging, small LD/LLDPE co-extruded film rolls treated at different wattages were kept in a humidity cabinet at a temperature of

$40^{o}C \pm 2^{o}C$ and 90% ±2 % relative humidity under tight winding conditions. At specified time intervals, the spools were taken out and samples were collected for inspection of treatment levels. The spools were further placed in the humidity cabinet and samples collected at stipulated intervals. This process of aging was continued for about 700 days and the observations are depicted in Figure-4.9.

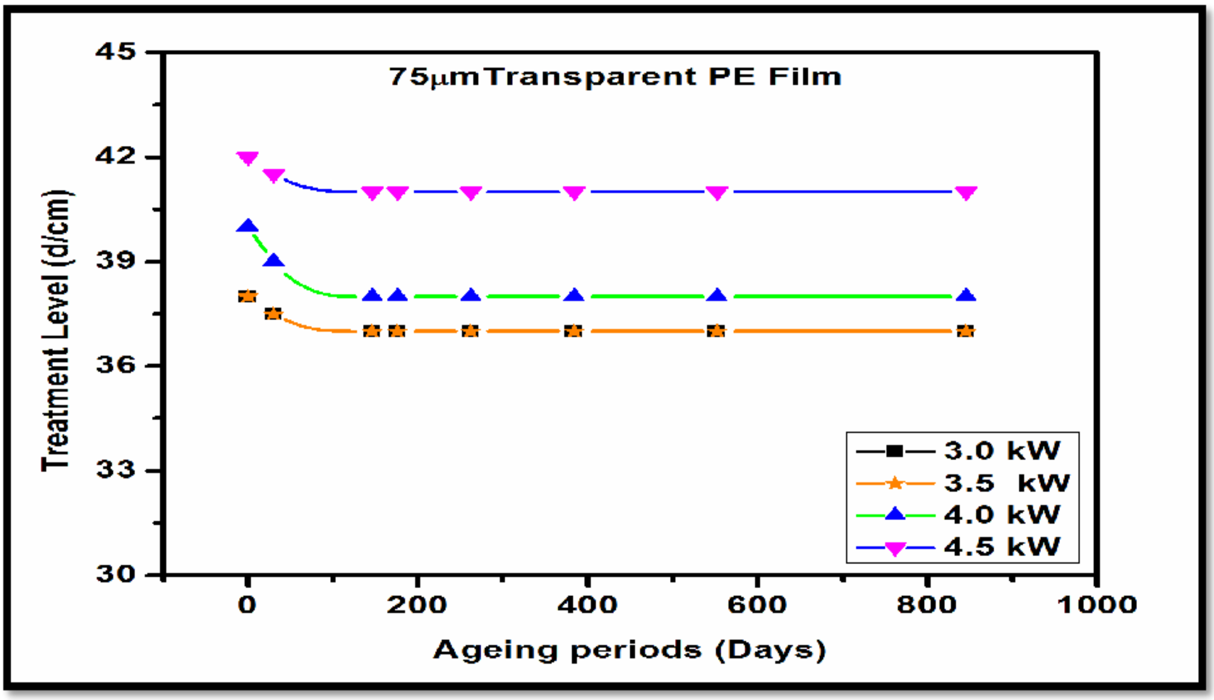


Fig-4.9: Effect of Ageing on Surface Energy of the 75µm Transparent LD/LLDPE Film.

In all the cases, it was quite apparent that after an initial small reduction in treatment level within about 180 days, the treatment level values reached an equilibrium stage and became asymptotic. It was noted by zuzanna Zolek-Tryznowska et. al. **[22]** that after 90 h of thermal ageing the total surface free energy dropped from 51.0 mJ/m^2 to 42.6 mJ/m^2 for LD/LLDPE film which was approximately 16%. After this decrease the value remained almost constant. It was quite interesting to note that irrespective of the variations in the initial level of treatment attributed to the range of applied voltages; almost all the samples attained a constant steady value which did not undergo any changes over a long period of time under observation. The common inference is that the treatment level decays with time **[22]**. Film surfaces immediately after treatment essentially causes dynamic surface migration of additives and low molecular weight materials to make the treated surfaces liable to undergoing continuous changes until a new equilibrium is reached. This change imparts lower surface energy to the surface. This lowering of surface energy is attributed to three main reasons; migration of small additives (mostly slip additives) on to the treated surface and covering of the reactive sites, interaction of the chemical groups present on the surface or interaction between surface moisture and the chemical groups.

The extent of decay was dependent on time and the initial level of treatment **[23-25]**. D. Markgraf **[26]** reported that besides other physical parameters like temperature, pressure, and relative humidity, the greatest cause of surface treatment decay was the migration of slip additive. In the present case, the decay of surface energy was found to be arrested after an initial small drop. The initial decay was attributed to the change in surface chemistry which was inevitable because of the interaction of the functional groups generated due to corona treatment and the surface remaining dynamic at the initial stages as explained above. However, the major decay which was attributed to the migration of the slip additive as per the theory proposed by M. Markgarf **[27]** appeared to be inhibited due to very slow diffusion or migration of the slip additive only, present in the farthest third layer through a three layered co-extruded film structure. The two interfaces moreover might act as a stiff hurdle to the migration process for additive.

4.2. Effect of Corona Treatment on Surface Properties of Co-extruded Titanium Dioxide (TiO_2)-Embedded Opaque White LD/LLDPE Films

The current study highlighted the influence of titanium dioxide ($TiO_{2)}$ on the level of charge development at the different applied voltages employed for corona treatment and its consequences on different surface properties. An attempt had been made to find suitable correlations of such properties and morphologies developed thereof.

Polyethylene (PE) films play a major and dominant role in the field of packaging. Either as an unsupported (monolayer) or in the form of a composite multilayered structure PE film can be made to serve a wide range of purposes. The LD/LLDPE films fabricated from virgin granules give a transparency of 100% light transmission and provide a see-through effect when used as a packaging layer. However, when used as an unsupported / monolayer, it fails to protect the light-sensitive contents inside the package from the deleterious effect of sunlight namely rancidity and bacterial putrefaction. In such cases, the transparent PE films fail to provide the necessary protection for the contents inside them. Hence, it becomes imminent not to allow the sunlight to reach to the contents. Here lies the importance of using TiO_2-loaded film. TiO_2 was a good bioactive material having high mechanical and thermal stability, moreover, it is preferred for its non-toxicity and low cost **[28, 29].** TiO_2 scatters visible light most efficiently thereby imparting whiteness, brightness, and opacity. The effect of TiO_2, when impregnated in LD/LLDPE film on mechanical and wear properties had been studied by Kumar et.al.**[30]**. In a separate study, the influence of TiO_2 on the dielectric properties of TiO_2 loaded LD/LLDPE film was investigated by Frubing et.al.**[31]**. The uniqueness of TiO_2 includes a combination of a high refractive index (2.73—rutile grade) and a high degree of opacity which was observed in the visible range of the electromagnetic spectrum. Among all other opacifying agents namely Silica, $CaCO_3$, and China Clay, TiO_2 appears to be the most efficient even at low doses. The degree of opacity offered to the transparent film depends on the type and doses of TiO_2 used. This type of film can also mask to some extent the oily or greasy appearance of any product as it resists light to pass through. Moreover, the shiny white opaque background provides a good surface for printing which in other cases was to be imparted by giving a white coating over the film surface. PE has extremely low surface energy which made it unsuitable for coating, printing and adhesive application. Different standard techniques such as flame, chemical, and plasma treatments were usually employed to increase its surface energy **[32-35**]. This develops wettability and spreadability, the two most essential characteristics for proper adhesion of any coating medium and also to achieve good lamination peel bond strength **[36].** However, corona treatment happens to be the most versatile and established method followed in industry to achieve higher polarity of surfaces **[37-39],** an essential criterion controlling the spreadability and wettability **[40, 41].** It was based on electric discharge under a substantially high potential difference between two asymmetric electrodes producing plasma—a highly reactive gas that contains ions, radicals, and also reactive ozone (they decompose into O_2 and active nascent oxygen) which interact with the surface and increases the surface polarity **[42]**. It is believed that the plasma gas reacts with the polymer surface primarily by breaking the H–C bonds and mostly the occasional tertiary hydrogen atoms are affected first, producing polar groups, namely, hydroxyl, carbonyl, and carboxyl groups on non-polar polymeric film surface **[40, 43-50].** These polar groups increase the polar component of surface energy which in turn helps to increase the overall surface energy. The corona treatment can cause micro etching leading to the generation of roughness **[51, 52**]. This roughness helps in improving the mechanical entanglement of the coating medium employed over its surface. Thus, this treated surface was capable of being either printed or laminated with other substrates. It has been observed that in industries, the polymer film surface is substantially wetted with printing inks, paints, coatings, and adhesives when the surface energy of the films is higher by at least $10mJ/m^2$ than that of the coating material [**53**]. In an earlier study by Bose et al. [**51**], a thorough investigation had been made by the authors on the influence of corona treatment with a transparent LD/LLDPE film in terms of the mode of development of surface energy as a function of applied voltage. The current study highlighted the effect of the extent of opacity generated when TiO_2 was incorporated in a transparent LD/LLDPE co-extruded film. The influence of TiO_2 on the level of charge development at the different applied voltages employed for corona treatment had also been discussed in detail. TiO_2 embedded opaque LD/LLDPE film also affected the barrier properties. It is worth mentioning here that no such thorough study had been done till date. Thus, the authors felt the urge to fill such a gap and prepare a scientific document for packaging industries.

4.2.1. Effects of Voltage on Surface Energy of Opaque Film

Figure-4.10 shows the variation in the level of treatments, that is, the change in surface energy of an opaque white LD/LLDPE co-extruded film (the surface containing the rutile titanium dioxide master batch, being exposed to the treatment in the discharge unit) with the changes in the applied load or Voltages. A very sharp increase in the treatment level was observed at the lowest limit of the range of applied load (3.0–3.5 kW) compared to that of an untreated surface of the same. A further rise in applied load had very little influence on the level of treatment. Rather a mild decrease in the treatment level was noted and an almost constancy in its value follows on subsequent increases in applied load.

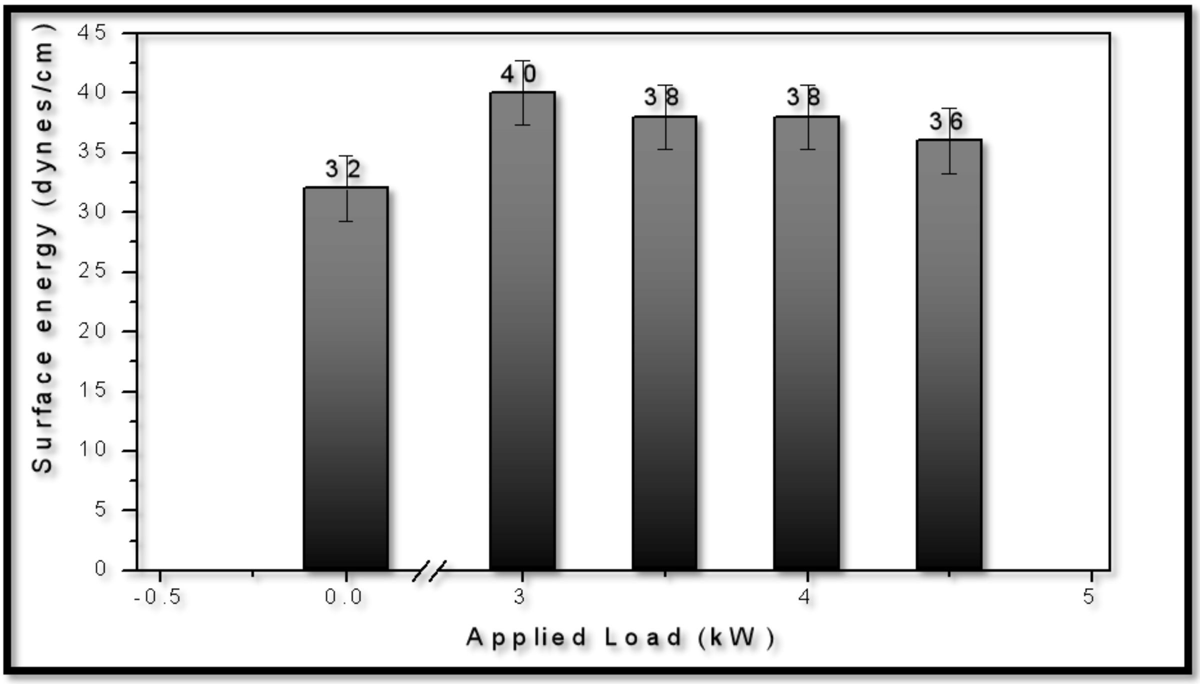


Fig-4.10: Surface energy versus applied load for a 75 µm milky white (LD/LLDPE) film.

The polyolefinic film surface had occasional C-atoms containing tertiary hydrogen atoms and these were liable to undergo oxidation very easily which in turn increased its polarity. In addition, the associated ionizing particles with their high energies (10–20 eV) augmented the process of oxidation **[54]**. The inertness in influencing the surface polarity, particularly at the higher voltages may possibly be attributed to the presence of finely dispersed TiO_2 particles on the surface of the film. The micro layer of TiO_2 might be expected to provide a conducting path to the static charges developed on its surface and mitigate its intensity to some extent. Secondly, it was thought that at higher wattages, there was an enhanced generation of energized active species like ions, electrons, and radicals, a substantial fragment of which became inactive in enhancing the polarity of the film due to mutual annihilation of the oppositely charged particles or the radicals among themselves **[55].** Furthermore, the presence of TiO_2 moieties helped to dissipate the static charges developed. Thus, the possibility of static charge generation was reduced remarkably as the voltage was enhanced. In an earlier section (4.1),**[51]**, it was shown that the polarity and hence the charge developed in the case of a transparent film (devoid of any titanium dioxide) undergone a steady increase with the increase in applied voltages. In this case, it is noteworthy that the rate of increase in polarity at the higher voltages, in particular, was far less than what was observed at the initial lower ranges of the applied wattages **[51]**. Moreover, a marginal decreasing trend was observed immediately after reaching the peak or optimum value. Hence, it can possibly be concluded that the presence of TiO_2 in the opaque white film helped to enhance the process of charge development at the lower range of the load applied on one hand while on the other hand, it did not allow the polarity to increase beyond an optimum at the higher voltages. It would possibly be worthwhile mentioning here that according to the MO (molecular orbital) theory, the band energy gap (between the valence band and the conduction band) for titanium dioxide was too low (3.2–3.5) eV to overcome even by the UV of Sunlight **[52]**. The average value of kinetic energy of the electromagnetic field during corona treatment amounts to about 10 eV and this enabled the electrons with energy higher than the binding energy to hit the TiO_2 microlayer and break the molecular bonds and caused the necessary surface modification **[42].** Thus, the energy available from the corona discharge process was substantially high to make TiO_2 conduct with the transfer of electrons from the valence band to the conduction band. The polyolefinic matrix is a well-known insulating material. Once the insulating matrix containing TiO_2 was subjected to corona treatment, the valence electrons undergone an elevation to the conduction band and attempted to reduce the insulating characteristics of the film. At the lower end of the load applied <3.0 kW or less, the insulating behavior still predominated over the conducting ones due to the lower number of electrons available in the conduction band. But at loads >3.0 kW, the surface charge density and hence the polarity steeply increased at still higher voltages as more and more number of electrons were available in the conduction band with more electron mobility, making the film apparently conducting. This leads to the process of simultaneous charge dissipation through several devices as mentioned earlier. Hence, no further increase in surface polarity and hence the surface energy occured at higher voltages under study. Hence, the permanence of the static charge developed due to corona discharge over the surface of insulating polyolefinic LD/LLDPE co-extruded film gets stabilized within the narrow range of applied voltage (3-3.5 kW) due to the presence of TiO_2, opacifying agent. Beyond this the electrons, it appears from MO theory that electrons in the valence band although become excited due to corona treatment were unable to reach conduction band and were available for doing the necessary chemical changes for static charge generation and in turn increasing the polar component of the surface energy (γ^p). At the higher voltages however the electrons were much more energized to reach the conduction band by virtue of which the charge developed gets an opportunity to get dissipated and hence, contributing nothing towards enhancing the surface polarity. In this way the surface charge density remains stagnant at a constant level in contrast to our normal expectation.

4.2.2. Effect of Surface Energy on Peel Adhesion Force of 3M Scotch Tape Adhered on Opaque White Film

The peel adhesion forces/peel bond strength of a standard scotch tape achieved on the surfaces of an opaque white film at different wattages is shown in figure-4.11. It was seen that the pull-off the force or the peel adhesion immediately undergone a remarkable increase for the corona treated surface with respect to that achieved on an untreated surface (which was not exposed to corona discharge) and even at the lowest level of wattages (<3.0 kW), the scotch adhesion was quite high.

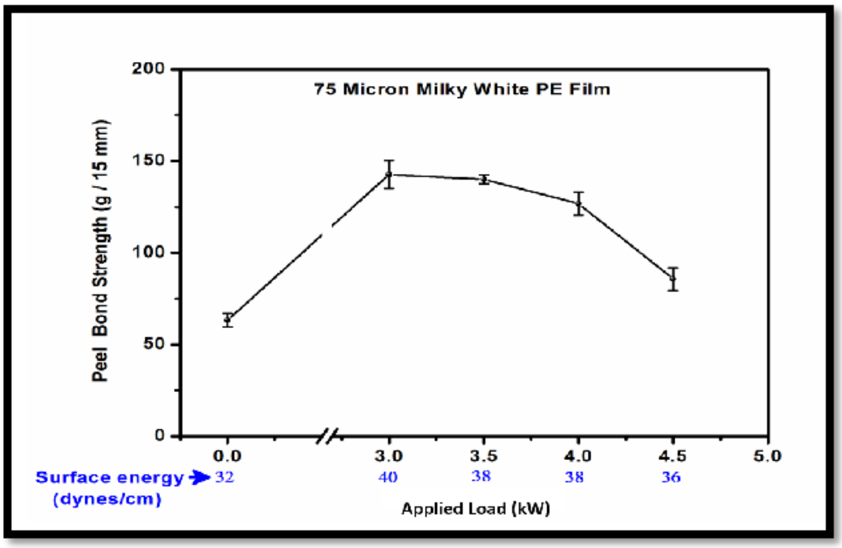


Fig-4.11: Surface Energy vs Peel Bond Strength for a 75µm LLDPE/LDPE Opaque White Film.

It might be noted that although the inner surface of the bubble during extrusion did not come under direct exposure to the treatment (considered untreated), still exhibited a peel adhesion force of slightly more than 0.323 kN/m. This might be developed because of some polarity generated during the extrusion of the film itself **[56]**.

However, on subsequent increases in applied wattages (>3.0–3.5 kW) a reverse effect was observed and the peel adhesion forces was found to decrease (within a limited range). This could perhaps be a direct consequence of the decrease in polarity with an increase in wattages applied as observed and thoroughly explained in the earlier section where a study on the variation in polarity and hence surface energies as a function of the applied wattage had been made. According to the JKR (Johnson, Kendall, and Roberts) theory **[3]**, the pull-off force observed was related to the thermodynamic Work of Adhesion, which in turn stood for the mechanical equilibrium between the energy released due to adhesion and the elastic energy stored due to the deformation of the contact zone. It could be readily perceived that in this particular case the energy released due to adhesion remarkably decreased at the higher range of applied wattage because of relatively lower polarity ascribed to the dissipation of charges, an observation which kept in conformity with the experimental results of the previous section.

4.2.3. Fourier Transform Infrared (FTIR) Studies of Opaque Film

FTIR spectra of the untreated film along with two treated (one being treated at 3.0 kW and the other at 4.5 kW) opaque white sample films of 75 µm thicknesses were subjected to FTIR studies and the spectra obtained were shown in figure-4.12. The films comprised ten pieces of three layered films made up of LD/LLDPE blend (the same blend was used in all three layers in prescribed ratios as shown in Table-4.2) in the Materials and Method chapter (Chapter-3.0). This was as per the suggestions of Kreidl et al**.[57].** White master batch in the mentioned ratio was used only on the treated or third layer of the co-extruded film. This layer was specifically devoid of any slip additive (EURECAMIDE). However, the same slip additive was used in the second and third layers, that is, the sealing layer of these three-layered co-extruded structures. It is imperative to mention here that in all the cases the treated surface was present as the reflectance surface while taking the spectra in the ATR mode. The asymmetrical stretching vibration peak of methylene (-CH_2-) appeared at 2915 cm^{-1} while the symmetrical stretching of the same group was indicated by the absorbance at 2847 cm^{-1}. The peak at 1463 cm^{-1} represented the deformation of methylene groups' perpendicular to the chain axis. The doublet at 730 and at 719 cm^{-1} confirmed the presence of Ti–O stretching vibration. However, the rocking of the hydrogen atoms in the methylene groups was also verified by the presence of absorption peaks in a similar region of the FTIR spectra. Small humps in the region of 3200 cm^{-1} for the two treated samples under consideration corresponded to the –OH groups. These were however absent in the untreated samples. The absorption peaks at around 1646 cm^{-1} indicated the possibility of the formation of a carbonyl (C=O) group which was formed due to corona treatment.

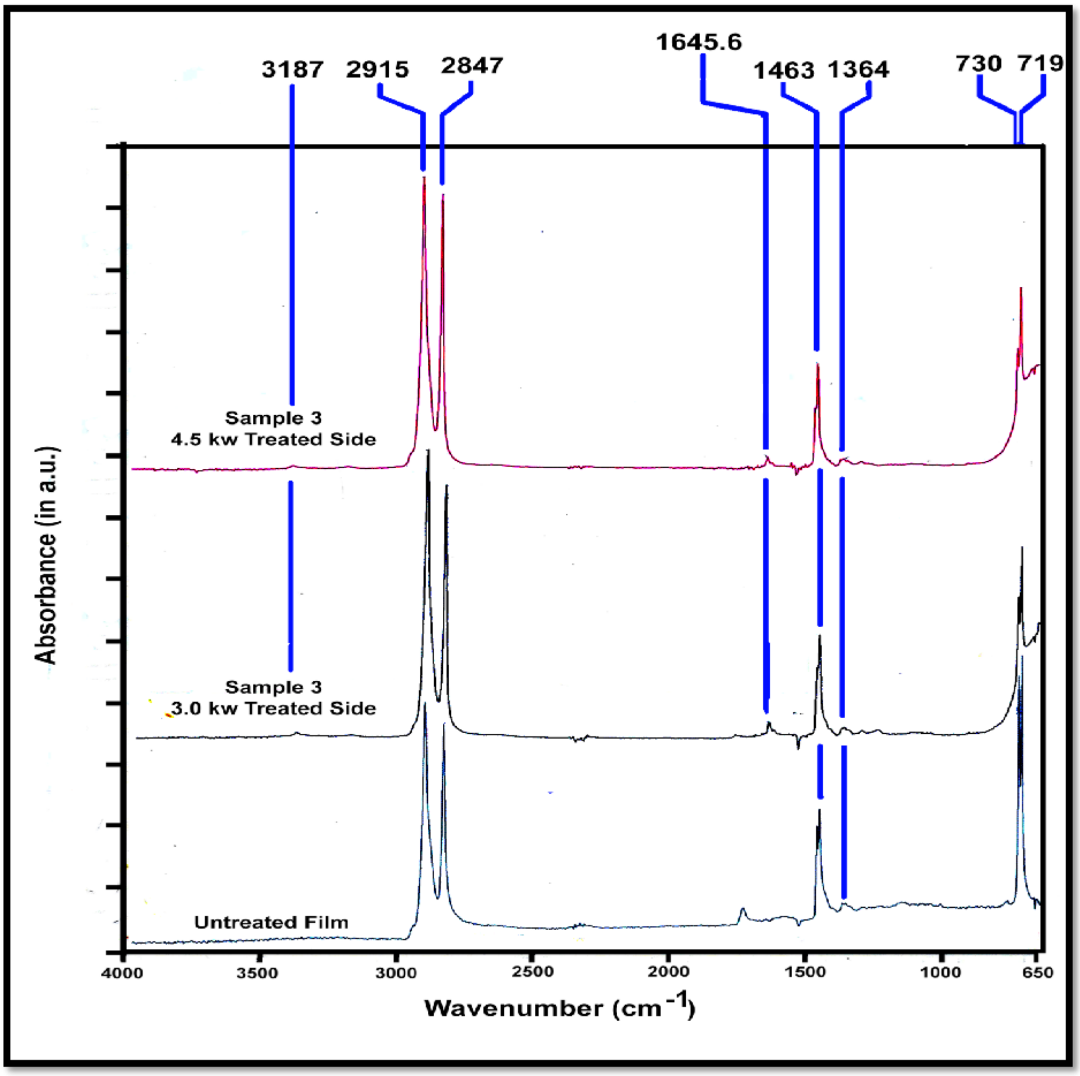


Fig-4.12: FTIR absorbance Spectra for the 75µm Untreated and Treated film with 4.5 kW and 3.0 kW Load at the Treater for 75 µm Opaque White film.

Similar observations were reported by Louzi et.al. **[57]**. It would be worth mentioning here that the opaque white film under investigation consisted of three layers in which the sealing layer contained an amide type of slip additive. This amide compound was supposed to exhibit IR peaks corresponding to both C=O (carbonyl) and $–NH_2$- groups. The C=O group generated on the surface of the film closely matched with the IR range stipulated for the carbonyl (C=O) of the amide, that is, 1646 cm^{-1}. Hence, it appeared that in the case of the treated films, both the carbonyl and amine peaks got superimposed on each other such that they became indistinguishable. Sun Christine**, [37]** in his review paper, concluded that in a typical industrial process of corona treatment elemental oxygen concentration varied from 10% to 18% depending on the level of energy density and the consequent introduction of polar groups on the film surface in the form of carbonyl, carboxyl, and other groups leading to surface energy in the range of 33–55 dynes/cm.

4.2.4. Effect of Voltage on the Heat Sealing Characteristics of Opaque White Films

In the work mentioned in section (4.0) by the same authors **[51]** a thorough study was made on the heat-sealing characteristics of corona treated transparent LDPE/LLDPE co-extruded film of identical thickness and composition. The present investigation had been undertaken so as to investigate the influence of Rutile TiO_2, as used in fabricating opaque white film on heat seal joint strength. Although the two surfaces of the same film developed different characteristics due to treatment on one particular side (the side away from the one containing slip additive), it was necessary to ensure an integrated, leak-proof, pilfer proof and uniform sealing. The sealed area must be strong enough to bear the mechanical hazards encountered during the formation of the pouch/sachet and others and also during the loading of the contents in it. The hot tack strength (strength during the filling of the pouch while the sealed area was still under hot condition), should also be reasonably very high. The mode of changes in heat sealing joint strength achieved with the opaque film is depicted as a function of applied wattage in figure-4.13.

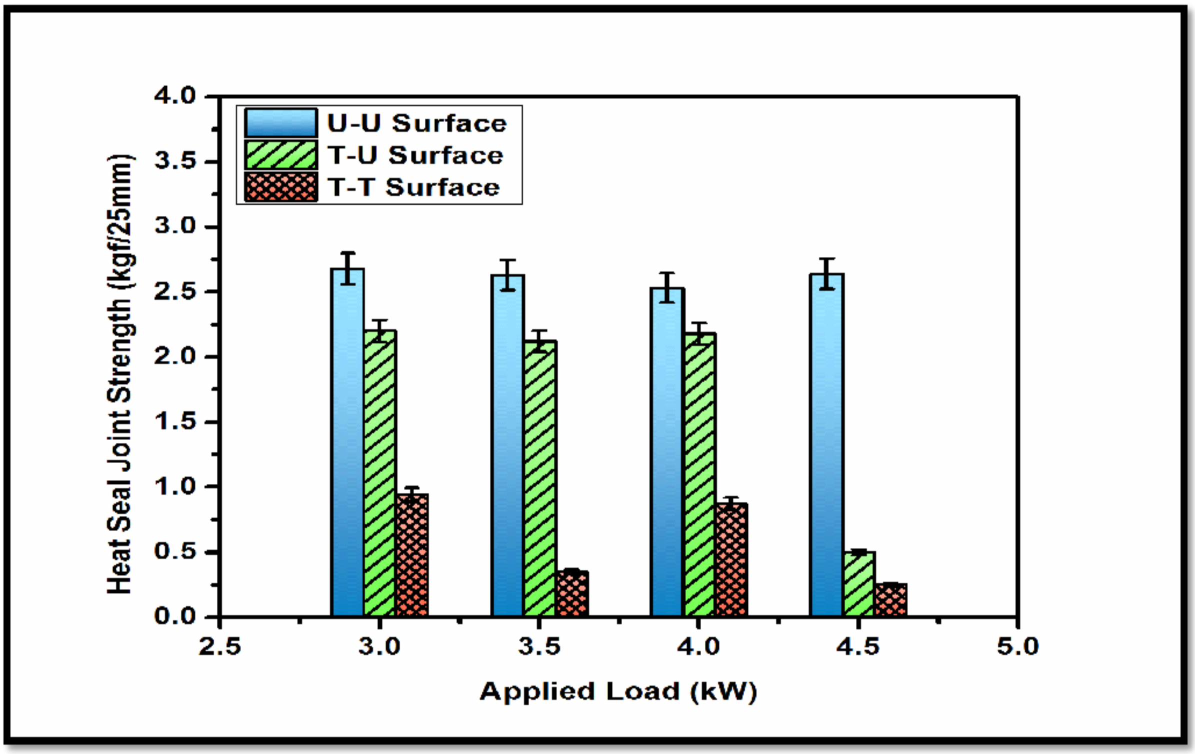


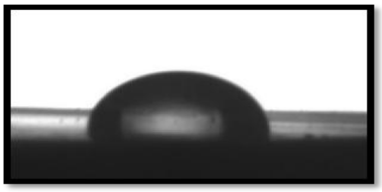
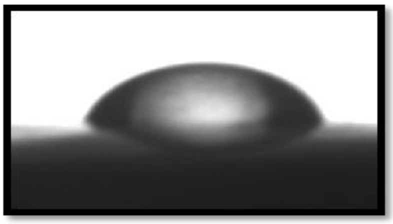
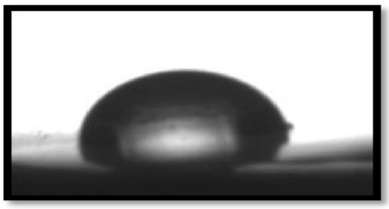
Fig-4.13: Variation of Heat Seal Joint Strength of the Opaque LD/LLDPE film with Applied Voltage

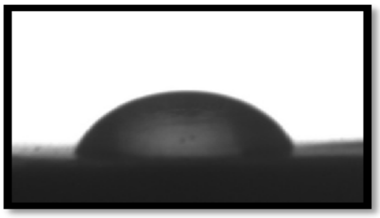
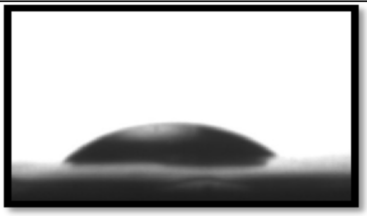
The patterns appeared almost to be the same as was obtained with the transparent film within the same range of load under study. At the lowest wattage (for treatment) of the range under investigation, all three different combinations of surfaces exposed for sealing exhibited the maximum possible magnitude of the heat seal joint strength (compared to the same for all other wattages applied). At any particular wattage, the heat seal joint strength changed in the order of untreated/untreated > untreated/ treated > treated/ treated surface combinations. For the untreated/untreated surface combination, there was a marginal decrease in heat seal strength with an increase in wattages in the range of wattage under study. It might be inferred that the strength of this particular combination of the surface was almost independent of the wattage at which corona discharge was conducted on the opposite surface. The seal strength of the untreated/treated surface combination steadily decreased with an increase in wattages applied. The treated/treated surface combination displayed an anomalous behavior in strength over the entire range of load and improper sealing was encountered in all the cases. In a TiO_2-loaded opaque white film, on sealing at a high temperature corresponding to the melting range of LD/LLDPE mixture, it can readily be perceived that the surface molecules of the adjacent layers (in the sealing zone) became mobile and were capable of diffusing mutually into the adjacent layers, the process of diffusion had come to an end on sudden cooling as is the normal process in any packaging industry. However, as the molecules of the sealing layers lost their mobility to come back to their original position, they were interlocked, on sudden cooling and hence, the necessary sealing was achieved. The extent of interlocking and hence the seal strength was strongly dependent on the extent of molecular diffusion which again was a function of temperature. In the case of the untreated/untreated surface combination the heat seal joint strength almost remained the same at all the voltages applied for corona treatment on the opposite sides of the film combination. Hence, for this combination of surfaces, it might be concluded that the heat seal joint strength was not at all affected by the level of treatment on the opposite side. The corona-treated Polyethylene films were hence, supposed to have macroscopic charged bilayers **[58]**. For the untreated/ treated and treated/treated surface combinations, we find a dramatic decrease in its heat seal joint strength, the latter surface combination showed the poorest strength. It is an established phenomenon that the surface being exposed to corona discharge undergoes oxidation and cross-linking as well which leads to an increase in molecular weight **[59]**. Hence, the oxidized surface inherited a higher melting temperature compared to the untreated surface. As heat sealing was carried out at a particular temperature of the sealing jaws under a definite pressure and dwell time irrespective of the nature of surface combinations, there developed a disparity in melting temperatures, particularly in the case of the untreated/treated surface combinations and relatively poor seal strength was obtained. Under those conditions, for the treated/treated surface combination hardly any sealing occurred.

4.2.5. Effect of Voltage on the Contact Angle of Opaque Films

Wetting and spreading characteristics are considered to be the most important parameters in packaging industries as the different types of adhesives, coatings, and printing inks used in such sectors are supposed to spread on the film under consideration. The contact angle was measured on the treated side of the opaque white film by observing the equilibrium angles formed by the conventional sessile fluid on its surface. The equilibrium contact angle formed on film surfaces treated at different wattages is presented in Table-4.3.

Table-4.3: Surface Characteristics of 75 µm Opaque White LD/LLDPE Film

Serial No	Sample Details	Contact Angle at the Treated Surface (Deg)	Surface Energy (Tension) (dynes/cm)	Images of the Contact Angle
01	Untreated Film	90±4	30	
02	Corona Treated with 3.0 kW Applied Load	60 ±2	40	
03	Corona Treated with 4.5 kW Applied Load	70±3	36	

Serial No	Sample Details	Contact Angle at the Treated Surface (Deg)	Surface Energy (Tension) (dynes/cm)	Images of the Contact Angle
04	Non-Slip Grade Film Corona Treated with 4.5 kW Applied Load	37±2	56	
05	Plasma Treated with Nitrogen	26±1	56	

For the sake of comparison, the contact angle and the corresponding surface tension achieved on corona treatment at two different wattages have been compared to the same parameters on an untreated surface of the opaque film in the said table-4.3. As in the investigation, the polyolefinic films were mostly made from polymer granules containing slip additive, an attempt had been made to inspect the influence of the slip additive on the contact angle and corresponding surface energy, by measuring those parameters on the surface of an opaque film made of plastic granules (of the same grade) without any slip additive of the same thickness. Moreover, the opaque film was subjected to the most modern technique of treatment (Plasma treatment with Nitrogen) to check the level of surface energy and contact angle that could have been achieved with the most modern technique of corona treatment. However, till such time this appeared to be too costly a proposition, particularly where commercial aspects were of major concern. It can be observed that the untreated side (the one which was not exposed to corona discharge exhibits an equilibrium contact angle slightly more than 90^0 and on treating at a wattage of 3.0 kW), the contact angle was greatly reduced to about 60^0 and there was an expected increase in surface tension by about ten units. It was quite interesting to note that on treatment at still higher wattage (4.5 kW), contrary to the normal expectation of further reduction of contact angle and a corresponding increase in surface energy, the contact angle however increased to about 70^0 (less than that available on untreated surface but more than that which was achieved on a surface after treatment at 3.0 kW) and became relatively more lyophobic compared to the one at a lower wattage. This observation kept in good conformity with the results of experiments on the effect of treatment at different wattages on other surface properties. The treatment with plasma however greatly reduces the contact angle with a concomitant increase in surface energy. It was worthwhile mentioning here that the presence of TiO_2 in the hydrophobic PE film helped to enhance the surface energy at the lowest wattage applied to a remarkable extent compared to the transparent (without any TiO_2) film of identical thickness and width **[51].** The presence of slip additive however acted as a deterrent in enhancing the surface energy and reducing the equilibrium contact angle. Hence, the presence of titanium dioxide in an opaque white film made the film quite sensitive to the corona discharge at low applied load or wattage and enabled it to develop contact angle and the consequent surface energy sufficient enough for printing and adhesive application. An excess of applied load particularly more than 3.0-3.5 kW had a reverse effect developing higher contact angle and in turn lowered the surface energy that was unsuitable for good printing and adhesive application, necessary for lamination. The explanations for such observations fall in line with those as had been detailed under section 4.2.1.

4.2.6. Effect of Voltage on Coefficient of Friction (COF) of Opaque Film

Case-1: Film to Metal Surface

The trend of changes in static and kinetic (Figure-4.14) coefficients of friction were observed when the treated side of the opaque white film was allowed to slide over a smooth iron metal surface in one case and over the untreated side of another opaque film separately in two different experiments, is depicted in figure-4.14. The observations were quite supportive to our earlier works (4.1) which included the variation in surface energy level, peel adhesion, and contact angle as a function of the applied wattage over the range of 3.0–4.5 kW. The opacity in the opaque film had been impacted by the incorporation of TiO_2 particles. Those acted as imperfections in the homogeneity of the film and provided roughness. As the percentage of TiO_2 was the same in the case of films subjected to different wattages of treatment, it might possibly be assumed that the roughness due to contaminants was almost identical in all the films. Corona treatment also was liable to produce some micro etching and hence roughness in the film. It could be expected that the extent of micro etching should have undergone an increase progressively with increase in wattages. From the earlier experiments, it was quite evident that beyond an applied load of 3.0 kW, a further rise in wattages hardly produced any improvement in surface energy, peel adhesion, and so forth. Either an anomalous change or a marginal decrease in the coefficient of friction was observed. In the present investigation following earlier observations, it could be expected that beyond 3.0 kW of applied load no appreciable change in the extent of micro etching should occur. Thus, instead of an increase in coefficients of friction, an almost constancy in COF was observed. Both the static and kinetic coefficients of friction, when the treated side of the film was subjected to slide over the smooth metal surface undergo a continuous decrease as the films treated at increasingly higher applied wattages were brought in contact with the metal surface. Secondly, the static coefficients of friction at any applied wattage remained always higher than the kinetic ones.

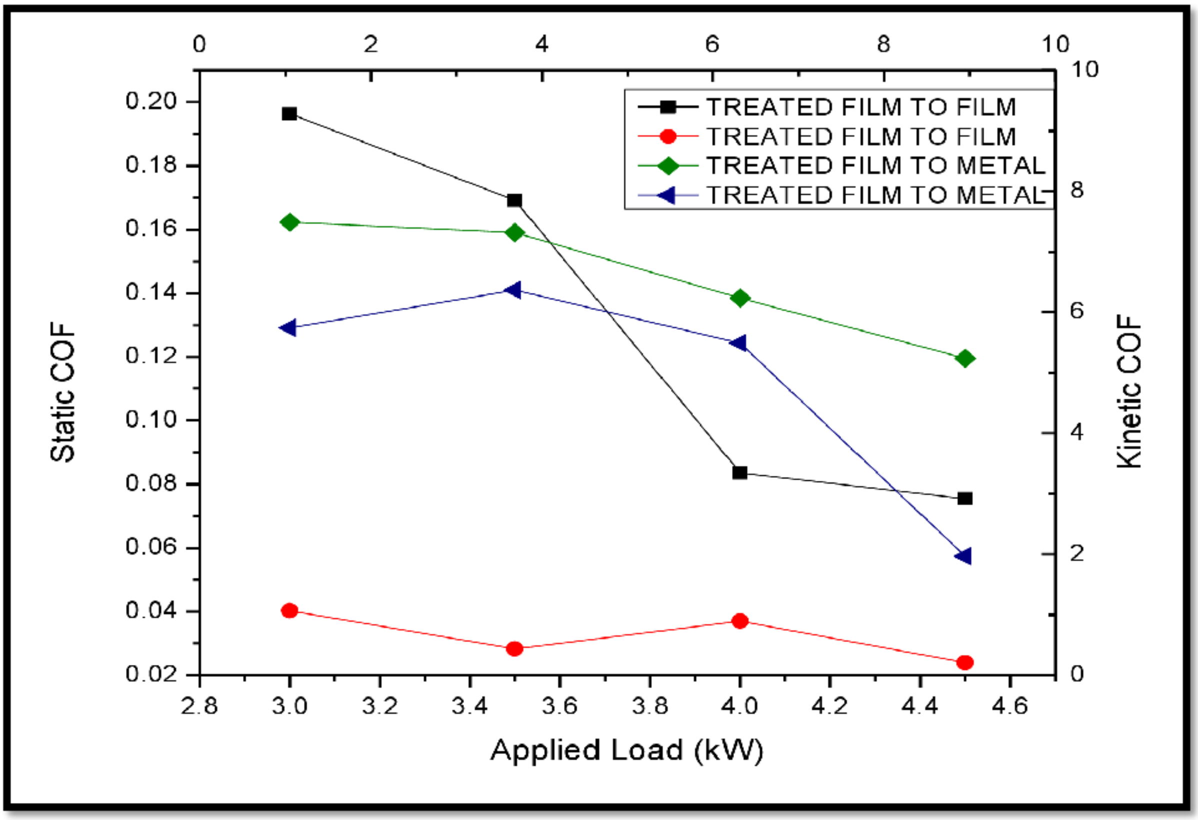


Fig-4.14: Variation of COF of Opaque LD/LLDPE Film with Applied Voltage.

Case-2: Film to Film Surface

When the treated surface of an opaque white film was subjected to friction over the untreated surface of another opaque film, both the static and kinetic coefficients of friction progressively decreased with increases in wattages at which the film surfaces were subjected to treatment. Under all circumstances, the values of static friction were always higher than the kinetic ones. In such case of film to film friction, both surfaces had impurities like TiO_2. The treated surface had micro etching besides the same content of impurities of TiO_2. Hence contrary to Case-1, the extent of friction was expected to be much higher. Hence, the static coefficient of friction was much higher than those for Case-1, particularly at relatively lower wattages.

4.2.7. Mechanical Properties of Treated Opaque Films

The mechanical properties of TiO_2-loaded opaque white film were compared to transparent film after corona treatment at two different wattages in order to investigate the influence of surface charges (if any) on the bulk properties of the film and are presented in Table-4.4. The mechanical properties such as elastic modulus, yield stress, breaking stress, % EB and tensile energy absorption of 75 µm opaque white film at two different wattages such as 3.0 and 4.5 kW were determined. It was quite apparent that such properties as mentioned above were hardly affected by electric discharge.

Table-4.4: Mechanical Properties of the 75µm LD/LLDPE Opaque Film before and after Corona Treatment on the film.

Before Corona Treatment:

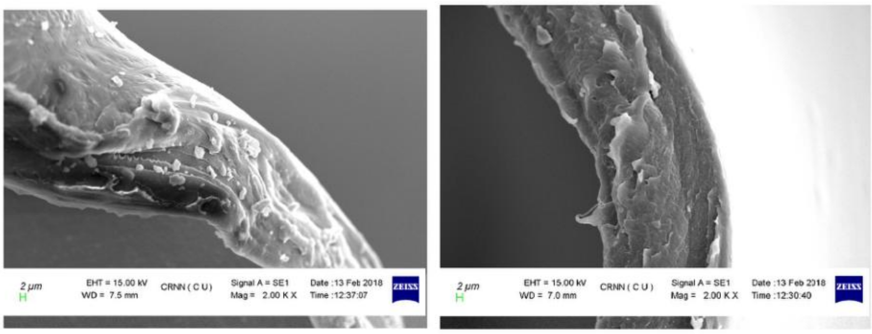
Direction	**Elastic Modulus (MPa) Tested as per ASTM D 882**	**Yield Stress (MPa)**	**Peak Stress (MPa)**	**Break. Extn (%)**	**Tensile Energy Absorption (TEA) (J)**	**Impact Energy (gm) Tested as per ASTM D 1709**	**Tear Strength (gf) Tested as per ASTM D 1004**
Machine Direction (MD)	159.0	12.2	23.4	652.40	8.9	410.0	1125.2
Cross Direction (CD)	168.8	11.7	22.5	658.4	8.4		1286.8

After Corona Treatment:

Direction	**Elastic Modulus (MPa) Tested as per ASTM D 882**	**Yield Stress (MPa)**	**Peak Stress (MPa)**	**Break. Extn (%)**	**Tensile Energy Absorption (TEA) (J)**	**Impact Energy (gm) Tested as per ASTM D 1709**	**Tear Strength (gf) Tested as per ASTM D 1004**
Machine Direction (MD)	160.7	11.9	22.6	648.0	8.5	415.0	1135.5
Cross Direction (CD)	166.8	11.8	22.8	665.2	8.6		1276.2

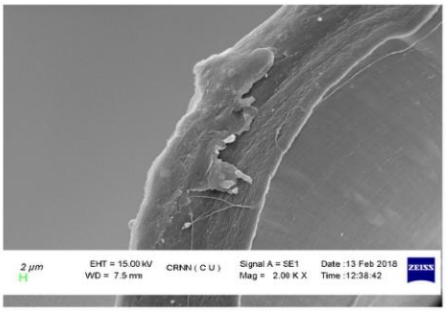
4.2.8. Morphological Observation

The surface morphologies of the corona-treated opaque white polyethylene films at two different wattages are shown in figures-4.15 a, 4.15 b, while figure-4.15 c shows the morphology of the untreated surface of the opaque film. It was well known that the surface reverse to the side where corona discharge was allowed to take place remained unaffected and showed the morphology of the original one **[58]**. Both the treated samples exhibited granular and etched appearances although the extent of etching varied depending on the wattages of discharge to which the films were exposed. The non-etched relatively smooth surface appearance of the untreated surface was quite relevant. However, the surface was slightly rough due to the presence of phase-separated TiO_2 particles which disturb the homogeneity of the film and produced roughness. Such appearance of the granular surface had been reported in the literature [**59**], wherein the extent of formation of the granular surface had been shown to be strongly dependent on the exposure time, temperature, and composition of gas formed during the time of exposure. Degradation of polyethylene molecules below an inert skin due to the gas evolved during the degradation process have accounted for the formation of such a granular appearance **[59]**. Occationally the local surface melting of degraded products leads to the formation of droplets encountered occasionally [**60]**.



a) 3.0 kW Treated Milky White LD/LLDPE Film

b) 4.5 kW Treated Milky White LD/LLDPE Film



c) Untreated Milky White LD/LLDPE Film

Fig-4.15: SEM (Scanning Electron Microscopy) Images of the Opaque Films.

4.2.9. Effect of Surface Energy on the Barrier Properties of the Opaque Film

The WVTR and OTR are two important and significant factors so far the packaging of perishable products by concerned types of films are concerned. Life cycle of the contents packed in pouches by the films are strongly dependent on these two characteristics i.e. WVTR and OTR. With the objective of determining these two parameters, tests were carried out over a period of time as per ASTM F 1249 and ASTM D 1434 respectively **[72,74]**. WVTR was determined in two different ways, (i) the treated surface of the opaque film exposed to water vapor and, (ii) the untreated surface of the opaque film exposed to water vapor. Films subjected to such testing were corona treated at 3.0 kW only. The WVTR computed for the first case was found to be 2.82 g/m^2/day while a value of 2.86 g/m^2/day was obtained for the second case (Figure-4.16 a). It was quite apparent that corona treatment had marginal or no effect at all on the water vapor transmission characteristic. Previous study **[51]** showed that the permeability of water vapor through 75 μm transparent film was 3.29 and 3.32 g/m^2/day for treated and untreated surfaces respectively. Hence, the presence of TiO_2 which acted as an imperfection in the homogeneous polyethylene film offered resistance towards the ingression of moisture through the opaque film of identical thickness. It could be assumed that the TiO_2 particles created a tortuous path in the film such that permeating water vapor was to travel a much longer distance in its path of permeation and reaching the contents, hence, the WVTR-value decreased quite appreciably in TiO_2-embedded opaque

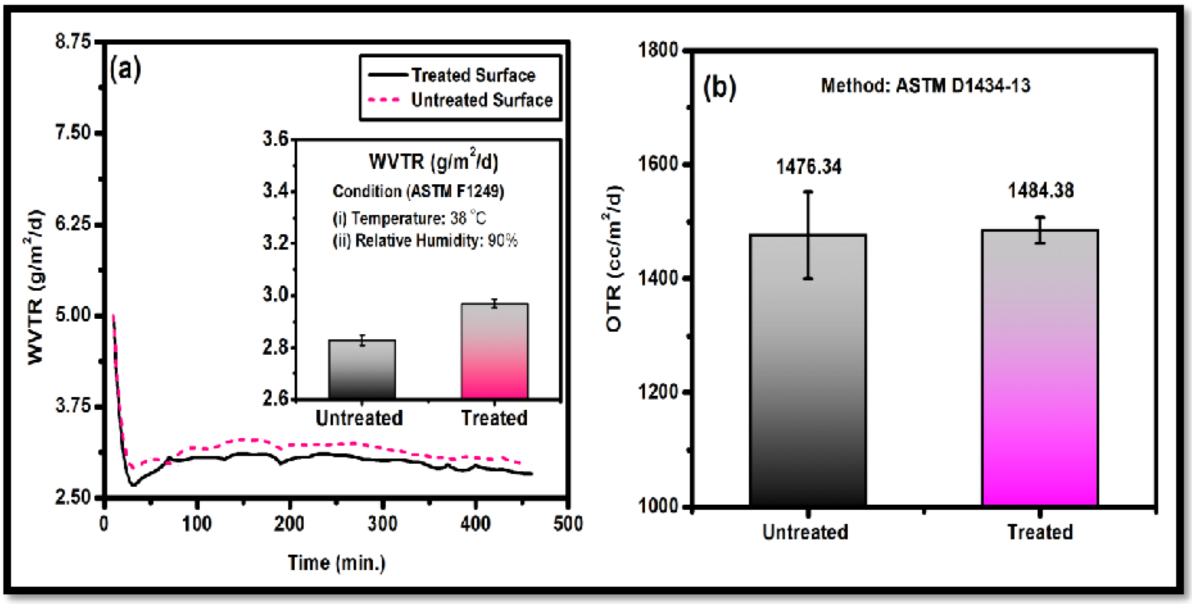


Fig-4.16: a) WVTR (Water Vapor Transmission Rate) b) OTR (Oxygen Transmission Rate) of the Opaque LD/LLDPE Films.

white LD/LLDPE film. This is a phenomenon that is bound to increase the shelf life of the packaged product in an opaque PE film. In a similar manner, figure-4.16 b showed the oxygen transmission characteristic of the 75 μm TiO_2 loaded opaque white LD/LLDPE film. The OTR was tested in a Gas and Permeability Tester, manufactured by M/s. AtsFaar S.P.A Italy. In the first case, that is, when the treated side of the film was exposed to Oxygen, the OTR value obtained was 1476.34 cc/m^2/day while in the second case; the same was computed at 1484.38 cc/m^2/ day. Here again, as expected the oxygen transmission rate was independent of the presence or absence of charges on the surface of the film.

4.2.10. Effect of Aging on of Surface Energy of the Opaque Film

Small rolls of LD/LLDPE co-extruded opaque white 75 μm film treated at 3.0 kW were put in winding conditions. The spools used to be taken out at specified time intervals and samples were collected for measuring the treatment levels. The spools were further kept in the cabinet and samples were collected at the time intervals same as that in the first case for over 800 days and the experimental results were demonstrated in figure-4.17. After an initial small reduction in the surface energy (with respect to the original one) within about 100 days was evident, afterward, the surface energy reached an equilibrium stage and became asymptotic. It was observed that the surface energy undergoes decay with time.**[18]** The surface molecules

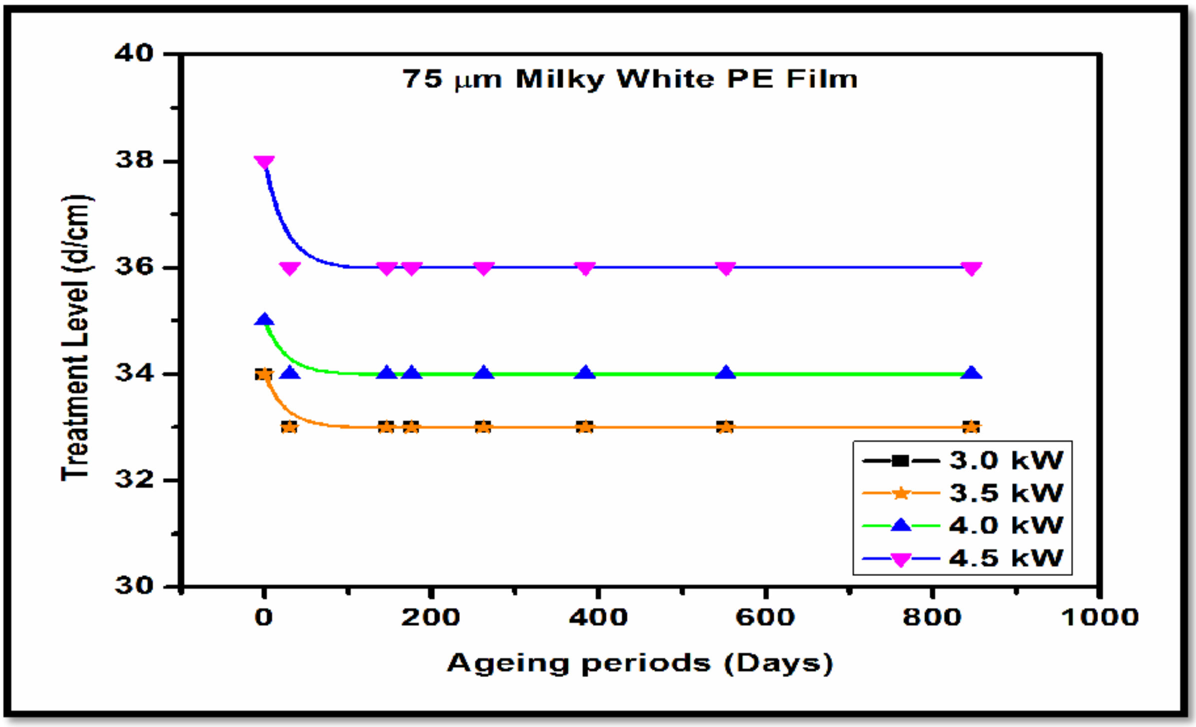


Fig-4.17: Effect of Ageing of the Opaque LD/LLDPE Films on Surface Energy.

immediately after treatment remained essentially in a dynamic condition. The migration of low molecular weight fractions and even the additives present in the polymer made the surfaces liable to undergo continuous changes until a new equilibrium was reached. This leads to the lowering of surface energy. In brief, the lowering of surface energy was caused by, the migration of slip additives onto the treated surface and covering the reactive sites, the interaction of the chemical groups present on the treated surface, and the interaction of moisture and chemical groups were generated due to treatment (mostly the ketonic and oxides). The extent of decay depended on time and the initial level of treatment, and so forth [**20,23,26**]. Markgraf [**27**] reported that other physical parameters like temperature and pressure, and relative humidity also can influence the decay of charge. It might be assumed that the presence of TiO_2 in the film deterred the above possible interactions. Those particles could have also produced a tortuous path for the migration of the additives to the treated surface.

4.2.11. Opacity and Whiteness of TiO_2-embedded Film

The extent of opacity generated when TiO_2 was incorporated in a transparent LD/LLDPE co-extruded film at a particular dose (master batch 7.5%) to inhibit the transmission of sunlight through it had been studied. Opaque white films are used for packaging applications where products sensitive to light and the whiteness developed in the films are used for the creation of aesthetics in the packaging. The results of the two said parameters in the case of present film are shown in Table-4.5.

Table-4.5: Test Results of Opacity Test as per ISO 2471 and Whiteness as per ISO 11475: 2017

Sr. No	Load applied for Corona Treatment on Film	Opacity (%)	Whiteness (WI) %
1	3.0 kW	99.70	82.96
2	3.5 kW	99.67	82.99
3	4.0 kW	99.64	82.41
4	4.5 kW	99.75	82.24

The more opaque the object, the higher the value of opacity. It was observed that the opacity and whiteness of the milky white LD/LLDPE films were independent of the voltages applied for corona treatment. Although different levels of treatment were obtained at different wattages, no change in either opacity or whiteness occurred. Thus, those two physical properties might be concluded as bulk properties and not surface ones. The level of opacity was 99% and the degree of whiteness achieved remained above 82%. These were quite sufficient values for desired properties in industrial applications, particularly for Packaging Industries.

4.3. Changes in Surface Energy on Inked and Subsequent Over Printing of Corona Treated Co-extruded Transparent LD/LLDPE Film

Commonly used substrates in manufacturing flexible packaging materials namely PE, PP, PVC and PET. All these are characterized by their chemic al structures and surface energies**.[61,62]** and suffer from the problem of low wettability properties [**63].**Wetting and adhesion of inks, coatings etc. on any film surface are associated with the nature of the substrates and the phenomenon of surface energy or surface tension.[**64].** Each film is characterized by their surface energies besides their unique chemical structure [**65,66].** The most common and the greatest drawbacks of these substrates is their low wettability properties. Interactions between the surface of the solid plastic film surface, the liquid element (i.e. inks, overprint varnishes, adhesives) and the resultant of surface treatments are dictated by the surface energy of the substrates and the surface tension of the liquids [**67**]. Printability is the main factor that controls high quality colour reproduction, increase ink gloss, uniform appearance without exhibiting any print defects [**68**]. In order to ensure good printability, the surface energy of the substrate and surface tension of the ink, varnish or lacquer should be at compatible levels. The surface tension of the inks must be lower than the wetting tension of the substrates to attain good printability, adhesion or ink lay down **[68,69].**

The Gravure process of printing /lacquering/varnishing is most commonly used in flexible packaging industries and the liquid gravure inks used for this purpose are formulated in such a manner that the inks getting released from the gravure cells properly wet the substrate, release the solvent very fast and on drying gives a very good scotch adhesion. The most important and critical parameters controlling the print quality include ink chemistry, nature of the substrate, surface treatment and ink transfer method **[51,70,71].**

The conventional gravure printing inks suitable for a particular substrate mostly consist of a suitable binder that binds the dried ink film on the surface, solvent or vehicle that carries the solid constituents including binding resin and colorant the pigment that gives the desired colour and other special additives (if required). The types of resin and solvent mostly control the surface tension of the liquid medium and the pigments are considered to have very little influence on it.

4.3.1. Coating Weights

An attempt has been made to inspect whether such variations in surface polarities have any influence on the solid deposition from printing inks or coatings. Five inks of different colour recommended for the PE films were selected and coated over all the surface across its width in a particular gravure printing machine with a given anillox.

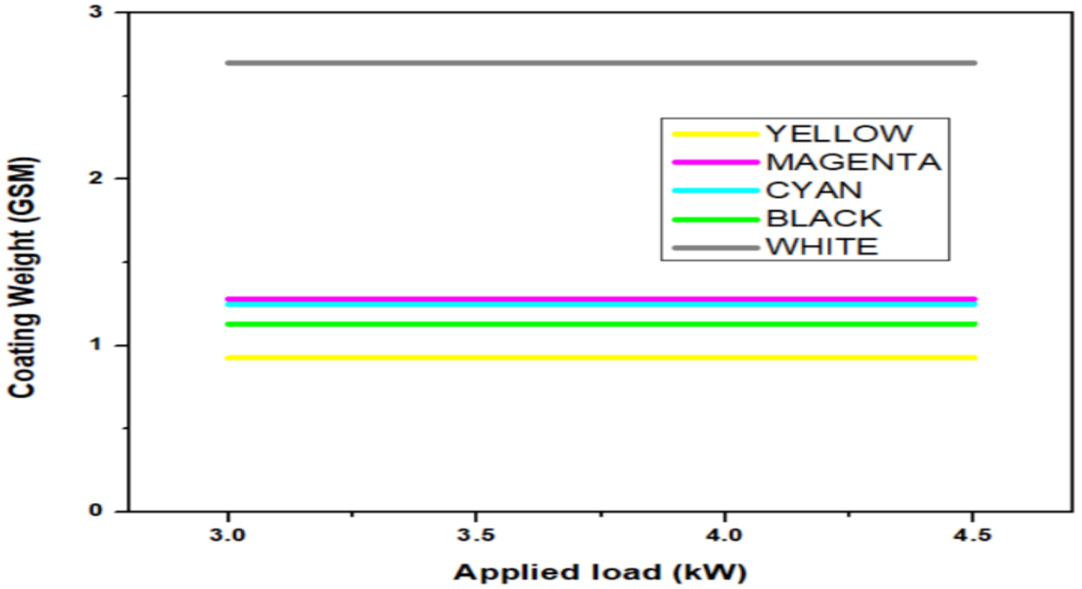


Fig-4.18: Variation of Coating weight of different inks vs LD/LLDPE films with different surface energy.

The inks had identical solids content (except the white) and viscosities within close ranges. The coating was accomplished with films having different surface energies. The respective coating weights achieved with six different coloured printing inks on film surfaces treated under different kilo Wattages are depicted in figure-4.18. As expected, the coating weights obtained with different colours varied within the range (0.925–2.7) GSM (g/m^2) irrespective of surface energies of the films the yellow showing the least and white, the highest surface energy in each case of surface energy of the ink film. Thus, it is quite apparent that coating weight available with a given anillox is independent of surface charges. Hence, with each ink the coating weight obtained on films treated at 3.0 kW (corresponding surface tension being 36 dynes/cm remains the same as available on films treated at 4.5kW corresponding surface tension being 42 dynes/cm.

It might be pointed out here that the increase in surface energies of the treated LD/LLDPE co-extruded film only helps in wetting and spreading of the liquid gravure ink which gets facilitated with increase in surface energy and has little or no influence on the amount of solid deposition. This is why the coating weights for any particular ink remain the same irrespective of the surface charges within the range under the study. It might be expected that at the interface of the ink films, the oxidized film surface and the corresponding ink film surfaces were involved in some interlocking through its chemisorptive / adsorptive forces. The polar asperities of the film surface were interlocked with the polar ink surface. The solid deposit of ink consists mostly of ground pigment particles and the medium or binder. The overall polarity and hence the resulting solubility parameter of the two surfaces appeared to match closely and hence the deposition became stable and gets anchored over there. In respect of the minor variations in coating weights as was observed amongst the inks of different colours it can be argued that the weight ratios of the Pigment: Binder varied within the range of colour under study. Under identical consistencies (viscosities), the binder remaining the same the pigment content underwent variations while interacting with the binder. The changes in PVC (pigment volume concentration) in respective inks might be the reason for such minor variation.

4.3.2. Effect of Voltage on Surface Energy of the Inked Film

LD/LLDPE co-extruded films were subjected to corona treatment at different wattages in tandem during its fabrication. These films were printed with different coloured inks and surface energies /tension over the printed surfaces were measured. The results were tabulated in table-4.6. It was quite apparent that the pattern of changes in surface energy with different colours remained almost unaltered irrespective of the magnitude of surface energy on the plastic coextruded film substrates. A few interesting phenomena was observed. In all the cases of inks the resulting surface energy values were always lower than the original surface energy of the treated films. This was because of only a film of lower surface energy could be wetted and spread over a surface having higher surface energy. Within the printed surfaces of different colours the yellow one possessed relatively higher surface charges (34 dynes/cm) while the ink films of other colours exhibited exactly identical surface behaviour (32 dynes/cm) irrespective of highest surface energy levels of the coextruded film. All the other colours gave ink films which were absolutely inert to the nature of the pigment and also to the type of initial pre-treatment over the original substrate film as the surface energy over the ink surface remained the same irrespective of colour. It will be worth mentioning that the determination of surface energy on a printed (inked) surface was quite relevant for those cases where reverse printing on the web/ substrate was done and same further processing like any adhesive or some special lacquer or coating application on the printed surface was needed. Thus for multicolour jobs all the different inks behaved almost identical fashion when the job demand a secondary processing or super imposition of colours on ink coated surface was required to get a definite design. Moreover the knowledge of surface energy on an ink coated surface was also important in making an ink/coating formulation as the surface tension of the formulated ink /coating must have to be less by about at least 10 dynes/cm than the surface energy of the printed surface over which it is to the applied. The selection of the ingredients and solvents for the coating needed to be made accordingly.

Table-4.6: Study of the effect of applied Voltage on Surface Energy/Corona Treatment level for different coloured ink coated on Transparent Polyethylene films.

Treatment level of PE film (kW)	Colour of Ink	Surface energy after printing (dynes/cm)
36	Yellow	34
	Magenta	32
	Cyan	32
	Black	32
	White	32
38	Yellow	34
	Magenta	32
	Cyan	32
	Black	32
	White	32
40	Yellow	34
	Magenta	32
	Cyan	32
	Black	32
	White	32
42	Yellow	34
	Magenta	32
	Cyan	32
	Black	32
	White	32

4.3.3. Scotch Adhesion of the Inked Films

The peeling forces achieved with different coloured surfaces of the LDPE / LLDPE co-extruded films undergoing corona treatment at different applied wattages generating different levels of treatment are shown in figure-4.19. It is worthwhile to mention that after printing or ink coating, the printed surfaces developed quite different treatment levels (surface energy) as already shown earlier. It was observed that the yellow inked surface attained relatively higher treatment level while all the other inked surfaces displayed quite uniform treatment level which was lower than the ink one. The yellow inked surface, although exhibited a surface treatment level of 34 dynes /cm on the inked surface over which the tape was pasted throughout the entire range of treatment level under study. Now showed a gradual and steady increase in peel bond strength with increasing pre-treatment level on the original PE film and achieved the highest bond strength when the original substrate, i.e. LD/LLDPE co-extruded film was treated at the highest load (4.5 kg) under study. A careful observation indicates that the lighter colour shades in spite of having almost identical coating deposits like Cyan, Magenta etc. provided relatively higher adhesion values compared to the darker ones like black, green etc. It could be readily observed from the figure-4.19, that the peel bond strength for every individual coloured ink film steadily increased with increase in applied load employed for corona treatment of the original LD/LLDPE film.

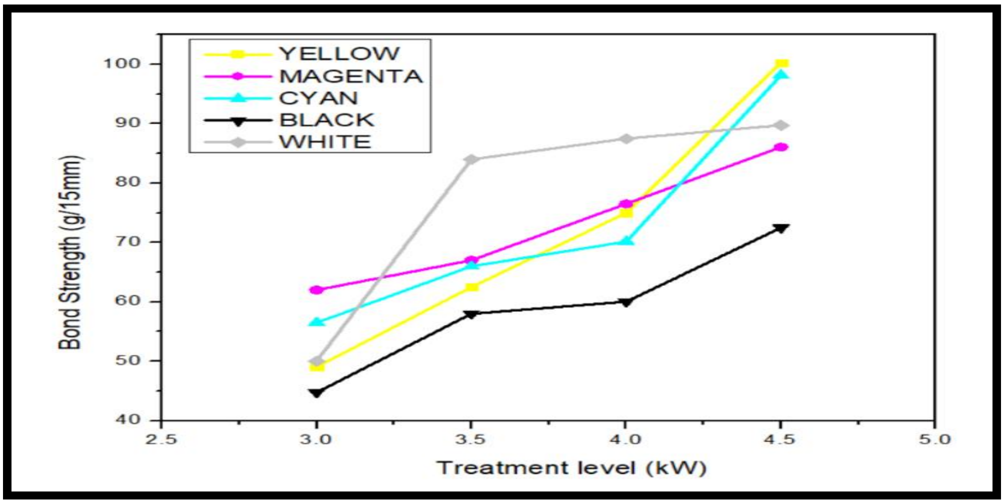


Fig-4.19: Scotch adhesion strength on different colour coated on LD/LLDPE coextruded film of varying surface energy.

This is quite expected as the surface energy of the film undergone a steady increase with it. It is also interesting to note that, on an average for any given load of treatment within the range under investigation the bond strength decreased in the order of white

>magenta>cyan>yellow>black of all the five colours under discussion. White had always the highest force of scotch adhesion and black the lowest one. The white ink in spite of having the highest solid deposition 2.7 g/m^2 (GSM) and hence providing a thick film appeared to anchor quite tenaciously to the substrate (treated PE film) with respect to other inks.

It might be inferred that the rutile titanium dioxide mostly used as white pigment in ink and coatings present in the dried film of ink might get involved in some sort of interaction with the polar functional groups (i.e. –OH, > C=O, -COOH, -O-O-etc.) on the corona treated film surface as all the other constituents of every ink remained the same except the pigment. In case carbon black used for pigmentation in black ink although there were functional groups capable of undergoing such interaction; a lowering of bond strength was observed as the tendency to from agglomerates and attaining a chain like structure, non-uniformity in structure size shape and pH of black particles might stand in the way of such interaction and hence resulting in such poor peel bond strength values. It was interesting to note that the force of adhesion of the ink films over the treated film lied in the order, white >magenta>cyan>yellow>black for any particular surface energy or applied load within the range of present study.

4.3.4. Effect of Voltage on the Contact Angle of Inked Film Surface

The Table-4.7 depicts a tabular representation of the variation in contact angle of the different coloured ink films deposited on corona treated co-extruded LD/LLDPE films. The film surface developed different surface energies due to the differences in applied loads. The variation in surface energies over the film surface helped to pull the ink film surfaces at different forces over it. The greater the pulling force the ink spreaded over the film surface more readily leading to an intimate contact between the ink film and the substrate film. The resultant of the three forces exerted by the surface energy of the substrate corona treated PE film, the surface tension of the fluid ink and the interfacial tension between these two led to bring the ink film at equilibrium after spreading at a definite contact angle. A smaller value of this contact angle gave an indication of the intimacy of the ink film with the substrate. It is readily understood as a greater intimacy led to development of more van der Waals' forces and in turn the forces of adhesion. The figure-4.19 can be considered as a replica of observations made earlier with the forces of adhesion with different inks.

Table-4.7: Details of Characteristics of Printing Inks used:

Film Details	Applied Load (kW)	Surface Energy (dynes/cm)	Color of Ink	Avg. Contact Angle (°)
Transparent PE film	3.0	36	Yellow	43.7
			Magenta	42.4
			Cyan	42.8
			Black	44
			White	41.4
	4.0	40	Yellow	38.4
			Magenta	35.6
			Cyan	36.6
			Black	43.6
			White	32.4
	4.5	42	Yellow	40.2
			Magenta	38.4
			Cyan	38.8
			Black	47.2
			White	35.5

The contact angle values were found to undergo systematic changes for each colour with the variation in surfaces energies of the substrates. Thus all the coloured films exhibited gradual decrease in contact angle with a concomitant increase in applied loads for treatment or in turn with an increase in surface energy of the film. Secondly for any given applied load the white ink showed the minimum value of contact angle and the black ink the highest one. The order of increases in the contact angle lied in the order white<magenta<cyan<yellow<black which was in accordance with the reverse of the order for forces of adhesion. The highest wattage considered in the present study (4.5 kW) always developed the highest surface energy, on the substrate and hence the least contact angles for all the inks under study. The changes in contact angle were within very close vicinity. However all the inks had reasonably good spreadability at the surface energies available within the range of treatment considered as all the contact angle was far less than right angle.

4.3.5. Effect of Voltage on Coefficient of Friction (COF) of the Inked Surface

The study on both static and kinetic coefficient of friction with the printed LD/LLDPE film (printing being carried out with different colours of conventional PE inks) might be very useful to the packaging industries particularly when the printed film was subjected to any further secondary operations like over printing (super imposition of colour), over coating or any adhesive application. In such cases, the printed surface was to pass over a large number of metallic (steel rollers) and in absence of a smooth sailing, development of scratch marks, lines etc. might take place. Hence there should be minimum friction between the printed surface and any metallic part that may come in contact.

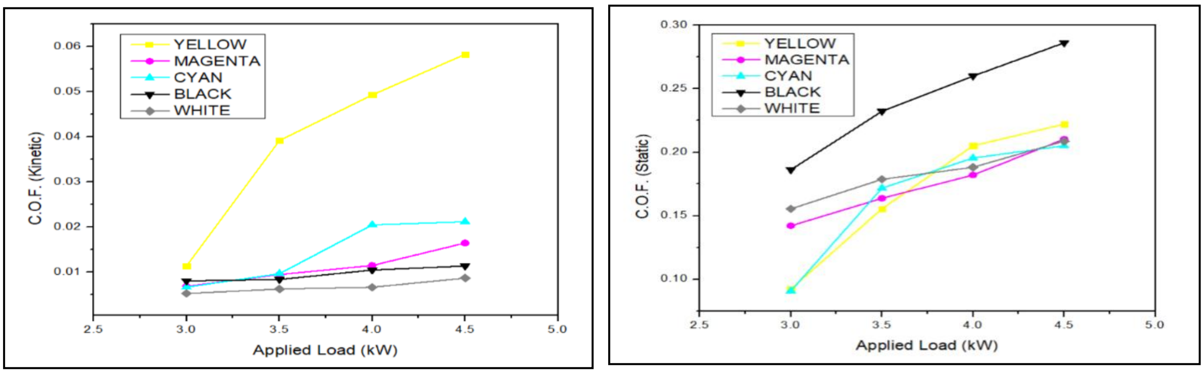


Fig-4.20: Coefficient of friction vs Applied Load on inked surface

The figure-4.20 displays the mode of changes in coefficient of friction (both static and kinetic) of the colour films as a function of surface energy developed on the subjected substrate at different applied loads (kW). The static coefficients of friction undergone a steady increase for all the coloured (different pigmented) inks over the entire range of surface treatment under study. The static COF attained its maximum values at the highest level of surface energy of the substrate irrespective of the colour of the inks. It might be argued that the higher level of surface treatment at high applied wattages might develop lot more of micro etching or indentations on the surface. The liquid inks by virtue of its flow-ability conformed to the contours of the substrate surface and its morphology. Thus the COF increased with increase in applied load for treatment. The kinetic coefficients of friction as noted in all the cases of colours were substantially lower than its static coefficient of friction values when compared at the same surface energy (applied load). In each case of coloured film the kinetic coefficient of friction undergone very little increment with increase in surface energy level. The increase in micro-etching with increase in surface energy level hardly influenced the kinetic coefficient of friction.

4.3.6. Scuffing Characteristics of the Inked Films

Scuff Proofness - a measure of resistance on scuffing / rubbing over the printed surface of any film (LD/LLDPE co-extruded film in the present case) is an important and essential characteristic of any printed surface. Considering the possibilities of the printed surface of the film particularly the exposed printed one to undergo friction during subsequent processing (if any) when the inked surface undergone friction over a large member of static or rotating rollers, the coating was subjected to scuffing. If the coating was loosely held to the surface or the coating itself developed rough surface due to off gauge or wide distribution of pigment particles within, it undergone scuffing or abrasion and a consequent loss in coating material, a phenomenon which was manifested by loss in weight. The coated / printed substrate might undergone scuffing also during transportation of the same when it remained in tightly wound condition in a reel as the coated surface undergone frictioning over the uncoated surface. In order to inspect this quality of scuff proofness; samples of dimensions as specified in ASTM F 2497 [**72,74**] were cut with the help of a template and were put into the frame of scuff proofness tester with the printed surface exposed outwards.

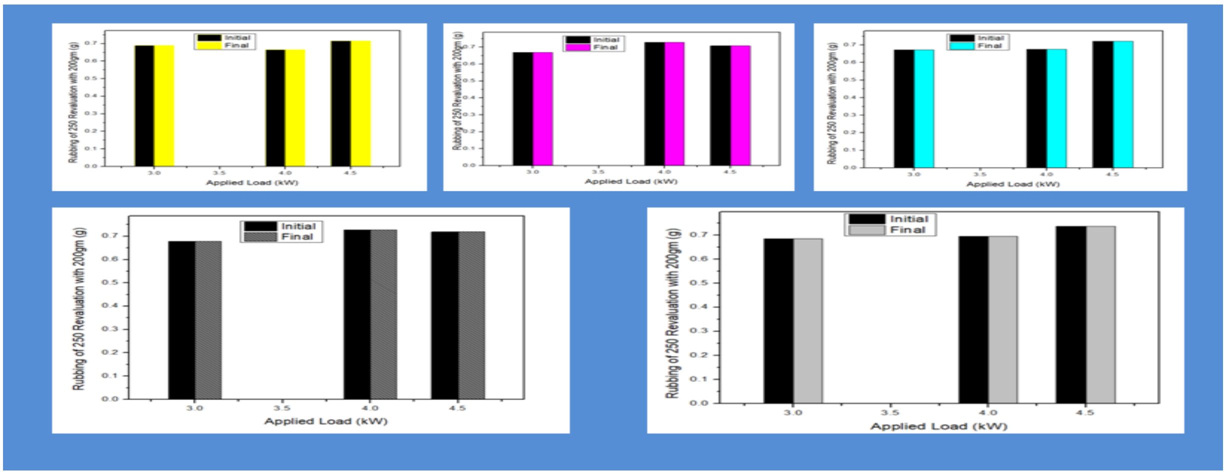


Fig-4.21: Scuff resistance of differently colored inks coated over co-extruded PE film at various applied loads.

Another circular sample of diameter (50 mm) was punched out from the same specimen and wrapped around a circular device which was capable of undergoing to and fro movement over the framed sample such that the printed surface of this interfaced with the printed surface of the other. The framed sample was weighed before subjecting the same to the test. The rotating circular device might be exposed with different loads, e.g. 50gms, 100gms, 200gms and 400 gms.

In the present work, experiment was carried out with 200 gms of load and was subjected to undergo 250 revolutions over the other printed specimen. After the stipulated no of revolutions, the sample was weighed again. This procedure was followed critically for all the colours under study. The performance was also investigated for all the voltages 3.0 kW, 3.5 kW, 4.0 kW and 4.5 kW at which the substrates were exposed for corona treatement for each individual coloured ink. The results have been shown in figure-4.21 by block diagrams as a function of wattages employed for treatment where two blocks for each colour (one representing for untested and the other for tested sample) have been shown adjacent to each other). Interestingly, irrespective of colour or wattages employed for treatment within the range under study, no change in weight was observed. It means that the abrasion resistances developed even at a voltage as low as 3.0 kW are sufficient enough to resist frictional losses under stipulated conditions. Hence it is difficult to reach to a conclusion from the above study within the limit of revolution and load of the experimental equipment. However, scuffing at higher revolution and higher load might be studied with higher generation equipment for effective conclusion.

4.3.7.Barrier Properties of Printed/Coated LD/LLDPE Co-extruded Films Pre-treated at Different Wattages

The barrier properties in terms of water vapour transmission rate (WVTR) and oxygen transmission rate (OTR) of the inked LD/LLDPE co-extruded films were graphically represented in figure-4.22. The ink coating formed a very thin microlayer over the LDPE films (corona treated) at a given (4.0 kW) wattage.

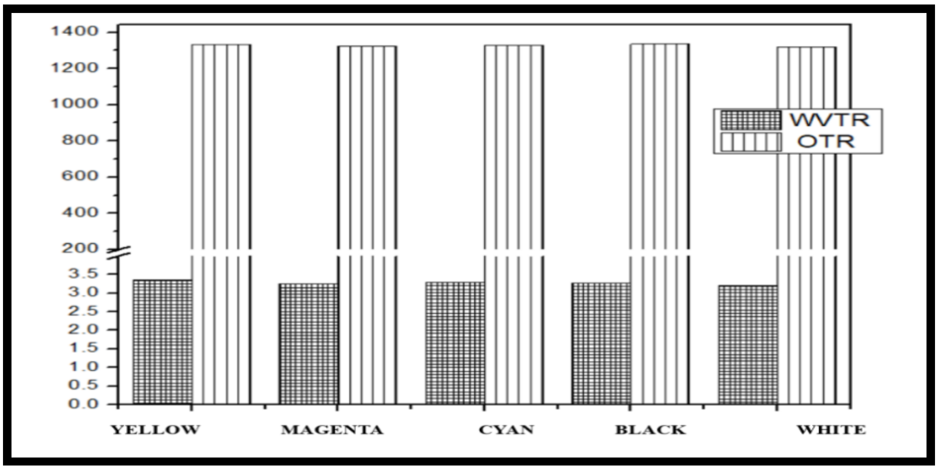


Fig-4.22: OTR and WVTR values for different coloured films.

In an earlier study the same barrier properties were investigated **[51]** with transparent LD/ LLDPE films treated at different wattages. In that case it was observed that these two barrier parameters namely WVTR and OTR were independent of the applied voltage or surface energies. From the block diagram it could be observed that irrespective of colour both the WVTR and OTR remained unaltered. Thus, the thickness of substrate and its composition remained the same and the coated ink microlayer hardly affected the barrier characteristics under suitable physical conditions.

4.3.8. Mechanical Properties of Ink Coated Pre-treated (Corona Treatment being done Before Ink Coating) LD/LDPE Co-extruded Films

The mechanical parameters namely elastic modulus, yield stress, peak stress, elongation at break, tensile energy absorption, tear resistance and impact energy of the said film were compared before coating and after coating. The same study was undertaken with samples in both the machine direction (MD) and transverse or cross direction (CD). Each of the mechanical properties as mentioned above was found to be almost identical when the values before printing and after printing were compared. Thus coating layer of white ink film over the corona treated substrate of LD/LLDPE film had little or no influence on the mechanical properties of the film. This might be because mechanical properties were considered to be bulk property whereas coating on any surface merely changed or modified the surface properties of the substrate.

Table-4.8: Mechanical Properties of the 75µm LD/LLDPE Transparent Film before and after Corona Treatment on the film.

Direction	Elastic Modulus (N/mm^2) Tested as per ASTM D 882	Yield Stress (MPa)	Peak Stress (MPa)	Break. Extn (%)	Tensile Energy Absorption (TEA) (J)	Tear Resistance (gf) as per ASTM D 1004	Dart Impact Test (gm) as per ASTM D 1709 before Treatment	Dart Impact Test (gm) as per ASTM D 1709 after Treatment
Machine Direction (MD) and Before Treatment	108.57	12.11	24.22	628.6	8.55	1072.25	419.50	419.00
Machine Direction (MD) and after Treatment	109.45	12.5	23.85	627.5	8.50	1073.00		
Cross Direction (CD) and Before Treatment	156.23	11.20	23.50	683.8	8.33	1236.75		
Cross Direction (CD) and after Treatment	155.75	11.50	22.85	684.0	8.35	1235.50		

4.3.9. Effect of Ageing on Printed Surface of Corona Treated LD/LLDPE Co-extruded Film

Printed films are used both as monolayers (unsupported) or in multilayers as per the specification demanded by the industries. However in both cases the printed film remains in tightly wound condition in a large spool form over some iron /plastic / paper core. In such cases, as the printed surface of the film remains in intimate contact with the unprinted one i.e. the surface away from the corona treated one and having much lower surface energy. It became necessary to inspect whether such intimacy has led to any deterioration in the surface quality and made it unsuitable for subsequent processing operations like batch printing in case of monolayer application or for adhesive application in case of lamination particularly for reverse printed laminate jobs. The problem becomes much more aggravated when the printed spool remains in Work-in-Progress (WIP) for a long period of time. In India the environmental conditions such as temperature and relative humidity (%) are sometimes found to have profound influence on the surface characteristics of such stored printed or coated film spools. In order to investigate such influences (if any) the LD/LLDPE co-extruded films coated with five different colours (being previously corona treated at 4.5kW) tightly wound in large no. of layers over a plastic core were kept in a humidity chamber maintained at 90 % ± 2 % RH and temperature of 40° ± 2°C for a period of four months. Samples of films were collected at regular intervals and the printed surface was subjected to surface energy testing as per ASTM - 2578 standards with freshly prepared dyne solutions each time **[72,74].**

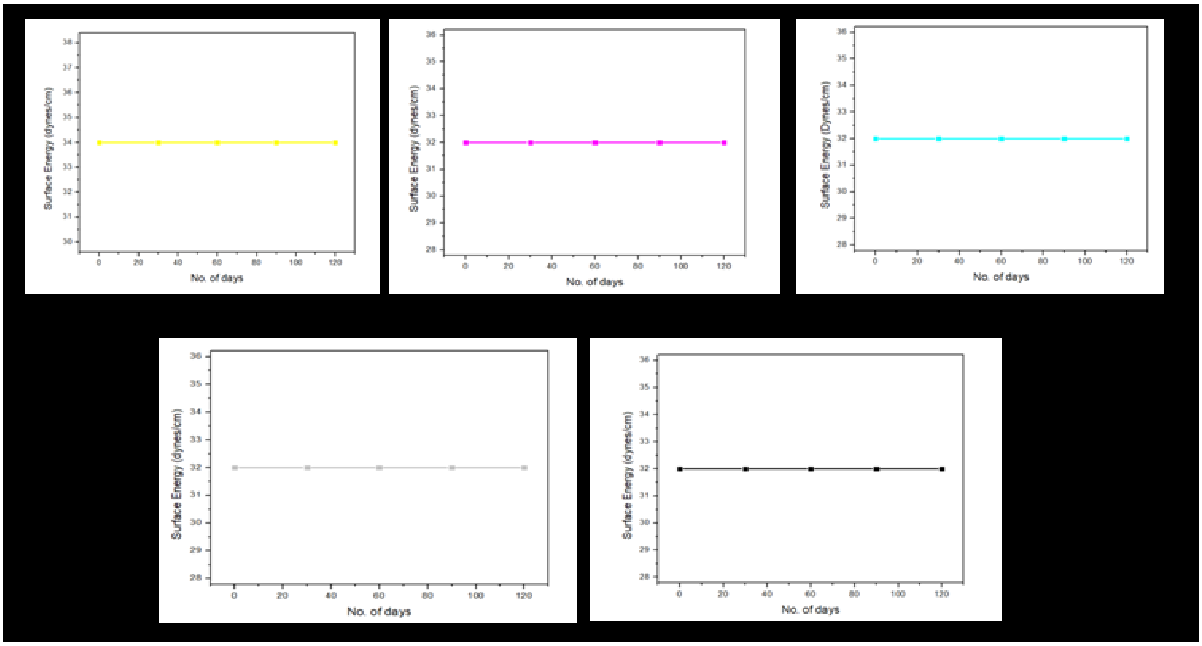


Fig-4.23: Effect of Ageing on Surface Energy for differently Colored Inks.

The test results were shown in figure-4.23. It is evident that no change in surface behaviour or surface energy occurred over the period scheduled under study. Thus printed or lacquered LD/LLDPE co-extruded films can be stored in work in progress (WIP) without any change in surface energy for at least a period of four months as a matter of fact obtained from the study.

4.4. Effect of Corona Treatment on the Lamination Characteristics of Transparent and Opaque White LD/LLDPE Co-extruded Films Laminated with Commercially Available PET and BOPP Films of Different Grades

Lamination **[72,73,74]** is a process of combining two or more similar or dissimilar substrates so as to achieve an optimum combination of properties required for a particular application mainly for those cases where an individual substrate fails to impart those singly. For the present study LD/LLDPE Co-extruded film laminated with commercially available PET and BOPP films of different grades.

Normally, a film or substrate having good heat sealing characteristics lacks in clarity, transparency, printability properties and in turn the films possessing good printability and mechanical properties mostly required during printing and any other subsidiary processing operations where it needs to withstand lot of tension and stretching is found to be devoid of any sealing or barrier properties. Every laminant is unique in some of the attributes but is definitely weak or poor in some other features quite essential for the overall performances urgently needed for the particular application. Hence a prudent and judicious selection of the different laminants is necessary such that the potentialities of the individual laminant complement each other to have the optimum combination of properties.

4.4.1. Effect of Voltage on Peel Bond Strength of LD/LLDPE Co-extruded Films Laminated With PET Films

The variation in the peel bond strength of the laminates made from polyester and LD/LLDPE co-extruded films having different surface energy levels had been shown as a function of surface energy for each colour under investigation in figure-4.24. A few interesting observations were quite apparent. For each colour under study it could be concluded authoritatively that irrespective of colour when coating weights varying within close range, the peel bond strength increased linearly and progressively with increase in surface energies of the LD/LLDPE films developed on it due to corona treatment at different wattages. The peel bond strength achieved with the magenta coloured PET films showed the highest and cyan coloured PET showed the least among all the coloured PET films under study. For the highest wattage (4.5 kW) applied for corona treatment on the LD/LDPE co-extruded film it was observed that the peel bond strength for the different coloured PET films lied in the order Magenta >Yellow>Green>Cyan. The numerical values of green and cyan remained within very close range; 202 g/15mm and 195 g/15 mm respectively. In case of the lowest wattage applied for corona treatment (3.0 kW) the reverse printed magenta colour printed PET film exhibited the highest peel bond strength when compared to those for the other coloured reverse printed PET Films laminated to LD/LLDPE films treated with 3.0 kW. In order to find suitable explanations for such observations the laminate viz. reverse printed PET /adhesive / treated LDPE film may be structured as PET/ printing ink / adhesive / treated side of LD/LLDPE film. Now the peel bond strength under discussion may be considered as the adhesion between the ink layer over the PET film and the laminating or treated side of the LDPE film.

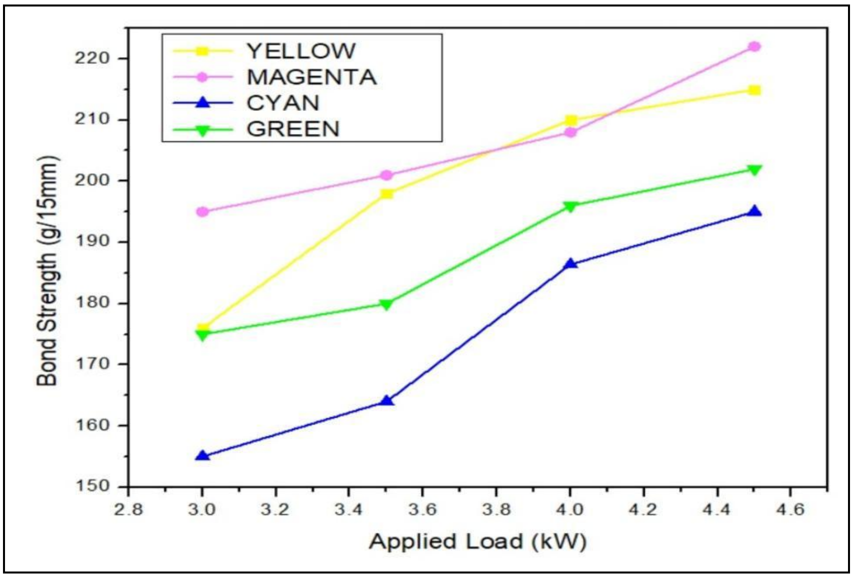


Fig-4.24: Variation of Peel Bond Strength at Different Applied Voltage.

The overall strength of the lamination or the peel bond strength is supposed to be composed of the following force elements. Force of adhesion of the laminate consists of the following components. Force of adhesion or adhesive force of ink over the PET film, interfacial force of adhesion between the ink film and the adhesive film, cohesive force of the adhesive layer, interfacial force of adhesion between the adhesive film and oxidized or corona treated surface of LD/LLDPE and cohesive force of LD/LLDPE. The algebraic sum of these force elements determined the ultimate peel bond strength of the laminate **[76].** However the weakest member of the above constituents determined or controlled the strength of the laminate. The normal mode of failure usually encountered during the peeling of such laminate usually occured through the interfacial surface of ink film of PET surface. The ink film getting transferred to the poly surface or in very rare cases through the cohesive failure of the poly layer undergone stretching while subjected to peel bond test. Thus the weak van der Waals' forces operating between the ink film and the substrate PET film might be assumed to be the apparent peel bond strength of the laminate. In the present study, all the coloured PET film displayed an interfacial failure and a clean transfer of the ink coating on the opposite side of the PE film. Thus the peel bond strength measured is the interfacial bond strength of the ink film on PET film and the bond strength values of all the colours laid within close range **[77, 78**]. Considering the thicknesses of the ink film (coating weight, solid deposition) remaining almost identical, the magenta coloured ink appeared to adhere on PET film more tenaciously than the other coloured printing ink. Under identical conditions cyan colour appeared to stick most loosely to PET film. The composition of all the inks used under this investigation was identical in all aspects except the colorant pigment, the differences in behaviour towards adhesion might be attributed to the pigment chemistry.

4.4.2 Effect of Voltage on the Study of Peel Bond Strength of Laminate Composed of Reverse Printed 12 µm PET Film (Coloured Side Laminated) With 75 µm Treated Co-extruded LD/LLDPE Opaque White Film

The results of the peel bond strength values achieved with different coloured PET films when laminated to opaque white LD/LLDPE films have been shown in the form of a block diagram figure-4.25.

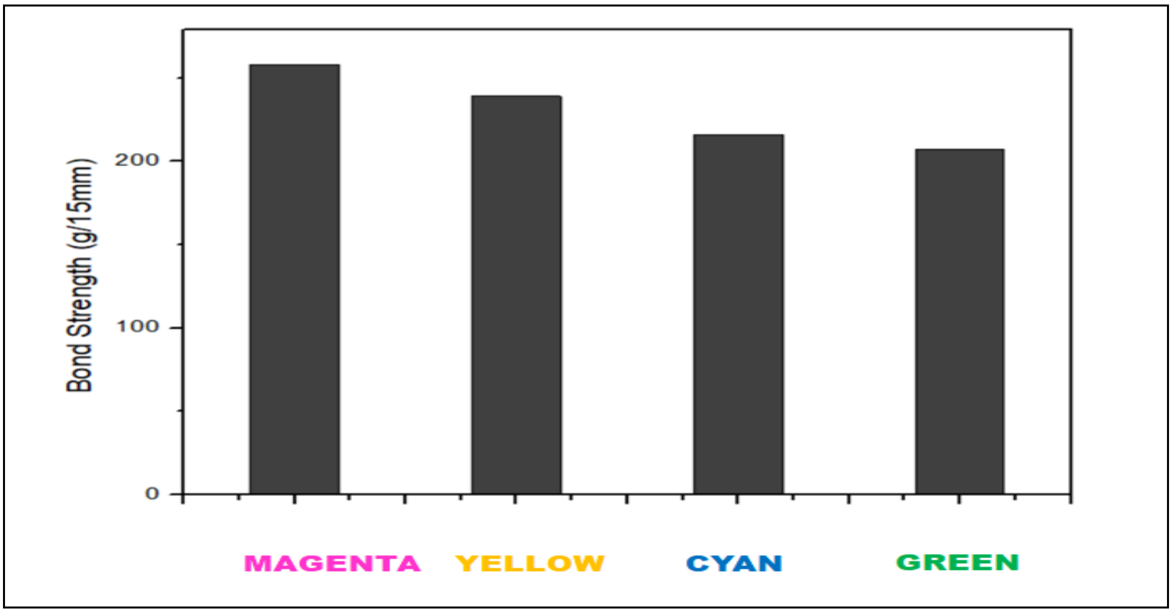


Fig-4.25: Bond strength vs Surface Energy of different coloured PET Film laminated with opaque white LD/LLDPE Co-extruded Film.

The changes in the peel bond strength values were observed to follow the same trend as was observed with transparent LD/LLDPE films i.e. the bond strength values was the highest for magenta and those with the green colour was the lowest. The overall trend laid in the order magenta >yellow>cyan>green. In this case also the mode of failure of the peel bond test was the same i.e. transfer of ink film from the PET side towards the LD/LLDPE side.

4.4.3. Comparative Study of the Peel Bond Strength and Heat Seal Joint Strength of the Laminates Composed of Commercially Available PET and BOPP Films with Treated 75 µm LD/LLDPE Co-extruded Films

The LD/LLDPE film used for the study had a surface energy of 38 dynes/cm.

From the table-4.9 below it is quite apparent that chemically coated PET had the highest level of surface energy on the coated side. All other films under discussions had the surface energy levels in the range of 38-41 dynes/cm.

Table-4.9: Conventional commercially available films and their surface energy on both sides.

Sample No.	**Type of substrate (film)**	**Surface energy (dynes/cm)**	
		Side-1	**Side-2**
S-1	12µm chemically coated PET (CCPET)	56	38
S-2	12µm plain PET	41	38
S-3	10µm plain PET	38	38
S-4	18µm natural BOPP	38	30
S-5	25µm natural BOPP	38	30

It might be mentioned here that the side with higher level of treatment (surface energy) is preferred for printing, adhesive coating and lamination. It is worth mentioning here that polyester is more polar than polypropylene. In most of the cases the PET film develops a surface energy of 38-40 dynes/cm during the fabrication of the film and no separate process of treatment is necessary, except in few cases a chemical coating is applied where extraordinary level of adhesive bonding is necessary. However, the chemical coating increases the cost of the film.

4.4.3.1. Study of Peel Bond Strength

The results of peel bond strength of the laminates fabricated by PET or BOPP and LD/LLDPE films have been depicted in the table-4.10.

Table-4.10: Peel bond strength of commercially available films laminated with LD/LLDPE co-extruded films

Sample No.	Peel Bond Strength (g/15mm)
S-1	768
S-2	320
S-3	334
S-4	202
S-5	234

The bond strength was found to be the highest for chemically coated PET where the surface energy was also the highest. For other two types of PET film the peel bond strength was within very close range. For the BOPP film (considered to be less polar and hydrophobic) the peel bond strength was much lower compared to that observed with the PET film although they were corona treated to the same extent as that on plain PET film. It may thus be assumed that the peel bond strength was controlled not only by the surface energy level but also the type of film; a polar film contributed higher peel bond strength than that offered by a non-polar film under identical conditions of treatment and other lamination conditions. It is well established fact that the force of adhesion or peel bond strength is dependent on the wetting or spreading characteristic of the bonding agent over those films involved in lamination and any other chemisorptive or physical adsorptive processes. One of the substrates being identical in all the cases under study (LD/LLDPE films) it was the other film (PET or BOPP) that played the dominant role in determining the peel bond strength. As the surface treatment level (38-41dynes/cm) of these two films remaining the same it was the chemisorptive forces between the films and adhesive that controlled the peel bond strength. In this regard the PET film being more polar, was supposed to give the enhanced strength.

4.4.3.2. Study of the Heat Seal Joint Strength for the Laminates

The results of heat seal joint strength are furnished below in table-4.11.

Sample No.	Heat Seal Joint Strength (kg/15mm)
S-1	9.71
S-2	8.84
S-3	8.96
S-4	5.41
S-5	5.64

Interestingly, the laminate made from the chemically coated PET showed the highest value of heat seal joint strength keeping in agreement with the highest value of surface energy of the PET film and the highest value of peel bond strength exhibited by the film and its laminate respectively. The two laminates fabricated by corona treated PET films having different thicknesses differed very little in their heat seal joint strength values as their levels of surface treatment were in close range. The values of heat seal joint strength were however lower than the laminates made from chemically coated PET. However the laminates made from BOPP films differing in their thicknesses but identical treatment levels displayed almost identical heat seal joint strength values which were substantially lower than those exhibited by PET laminates. The second substrate (LD/LLDPE) film with the same other physical conditions of lamination remained unaltered. It might be because the heat seal joint strength was dependent on the peel bond strength between LD/LLDPE film and PET or BOPP as the case may be. The greater the thickness of the sealant layer the greater would be the heat seat joint strength. When it is attempted to separate two laminate layers through the sealing layer, failure might occur either through desired layer or through the adhesive failure (peel bond) between the PET / BOPP film. The weaker of these two forces determined the ultimate heat seal joint strength. In most of the cases sporadic or scattered plucking of poly from the surface of PET or BOPP occurred. Thus it is a common observation that greater the peel bond strength greater is the heat seal joint strength.

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Chapter 5:

SUMMARY AND CONCLUSION

5. SUMMARY AND CONCLUSION

Corona Treatment has long been considered as an effective prerequisite of secondary operations like printing, varnishing & lamination on LD/LLDPE film packaging for the adhesion of printing ink, coating or adhesive by enhancing the polarity of such polyolefin films. There is a paucity of scientific research on surface treatment, corona in particular. In the absence of any standards, the use of Corona treatment in the current day industry is in jeopardy. In order to reciprocate to the call of the industry, a trial was made to study the influence of Corona treatment on such surfaces with varied magnitude aiming towards formulating standards of Corona treatment on LD/LLDPE films.

1. LD/LLDPE coextruded films (natural, transparent) was fabricated by blown film technology and subjected to in-line corona treatment at various applied loads. The changes in surface polarity and hence the surface energies of films were inspected with dyne solutions of different surface tension. The corresponding equilibrium contact angle was measured with the sessile fluid by a Goniometer. The contact angles and the surface energies of the films treated at different voltages were studied, keeping the amperage the same. The surface properties like scotch adhesion, coefficient of friction, heat-seal characteristics, surface morphology, and barrier properties with respect to WVTR & OTR were determined and compared with reference to untreated surface & amongst themselves for each applied load/voltage. The surface energies of the films were found to increase with the applied load initially at a fast rate and comparatively slow at higher voltages within the range under study of (3 to 4.5 kW).

At the higher end of the applied electrical load, the enhancement in surface energy was not substantial. Thus, it was suggested that an electrical load of 3.5 kW to 4.0 kW was most effective for producing the optimum surface energy necessary for secondary operations like printing, varnishing & lamination in the case of transparent LD/LLDPE films. The improvement in surface energy with an increase in applied electrical load was also evident by the scotch test & the changes in surface morphology as it was manifested by the extent of electing & surface roughness generation; a phenomenon that was reflected in the surface coefficient of friction. The heat-seal joint strength is however greatly affected by the formation of a polar oxidized surface on the treated side. Amongst the different combinations of surfaces such as untreated/untreated, untreated/treated & treated/treated, the combination untreated/untreated showed the highest heat-seal joint strength. In contrast, the treated/treated surface combination had marginal or no sealing characteristics. The plausible reason was attributed to the much higher softening temperature of the oxidized treated surfaces. The barrier properties of the films were hardly affected by such treatment. While studying the effect of aging on the level of treatment, it was noted that at the initial stage of aging upto 120 days, there was a marginal drop in the surface energy after which no considerable change could be noted. Hence it was concluded for the desired effect of corona treatment, higher wattage leading to higher electricity consumption was not advantageous.

2. Secondly, 75µ Co-extruded LD/LLDPE film was fabricated in a similar manner where a white master batch of titanium dioxide (TiO2) was added to the granules used as feed for the first & middle layer of the ultimate film. The third and the sealing layer contained slip additive but no TiO_2 master batch. Corona treatment was undertaken over the first layer following the same procedure as outlined earlier at different applied electrical voltages to develop different surface energies which were measured by standard dyne solutions & corresponding contact angles were checked by goniometer using sessile fluid.

It was observed that the maximum treatment level was achieved at the lowest wattage (3.0 kW). At the same time, further increase in electrical load hardly improved the surface energies further & there was almost a leveling off in surface energies, or in some instances, there was a marginal drop. The presence of TiO_2 moieties in the surface layer was accountable for this phenomenon.

i) PE being non-polar and inert, the static charge developed on its surface by the formation of ions and radicals due to corona treatment is supposed to remain on its surface itself. This happens in TiO2-loaded film at lower voltages ≤ 3.0kW.

ii) In case of higher electrical load, the ionizing particles of corona discharge having energies in the range of 10 -23 ev promote the electrons of the molecular orbital from the valence band to the conduction band & making the film somewhat conducting & allowing the charge to get dissipated. Thus, treatment above > 3.0kW appears to be of no use.

iii) The scotch bond test results fall in line with the above observations. The trend in changes of the heat seal joint strength followed the same pattern as was observed with transparent films. The mechanical, barrier, and aging characteristics of the films treated at different voltages keeping the amperage the same were found to be independent of treatment level.

3. Thirdly an attempt has been made to determine the state of the surface energy of the treated surface of the substrate (LD/LLDPE) film when covered with coating/printing ink. There is very little information about such surface behaviour of the coated film though it is very important as in the industry subsequent processing namely batch printing or adhesive lamination is done mainly over such film. It was noted that the surface energy over the coating surface did not vary or vary over a narrow range irrespective of colour, coating weight, and variation in the surface energies over the substrates (LD/LLDPE films) which were corona treated at different electrical loads. In all the cases of coloured films, there was a drop in the level of surface energies concerning the initial levels achieved over the LD/LLDPE film surfaces primarily by treating at different wattages. It is worth mentioning here that for obvious reasons, during subsequent processing like lacquering or application of adhesive, the surface energy of the coating solution is required to be less than that of the coated surface at least by 10 dynes on which it would be applied for proper wetting, spreading, and necessary adhesion. The other surface features like roughness/coefficient of friction etc. and even the bulk mechanical properties do not undergo any changes when compared as a function of the original surface energies of the LD/LLDPE film. The minor variations in contact angle hardly have any impact on respective surface properties.

4. Finally, the lamination characteristics of 75µ co-extruded LD/LLDPE with corona treatment at different voltages keeping the amperage the same were laminated with reverse printed (coloured surface being sandwiched) 12µ PET films were evaluated. The PET films were coloured with some standard inks for polyester. The influence of surface charges of the PE films over the peel bond strength between the coloured PET film and the treated surface of the PE film was very little. However, for a differently coloured PET film, some differences in the peel bond strength were observed for different levels of surface energies on the treated PE films. Among all the colours, the Magenta colour was found to exhibit the maximum peel bond strength values at the same wattage used for corona treatment.

Chapter 6:

FUTURE SCOPE OF WORK

6. FUTURE SCOPE OF WORK

During the course of this research work certain limitations were exposed which could not be covered in the study for some design restrictions, methodological constraints and limiting factors of the equipment used. It was strongly felt that in the current research domain, some areas remain unexplored calling for detailed future investigation. In this section, those areas are highlighted.

1. Aluminium foil packaging containing oil on its surface resulting out of its manufacturing process, for secondary operations warrants a prime coating to overcome the effect of oil. Detailed studies can reveal whether corona treatment might be a cost-effective alternative to this coating practice.

2. It was observed that the surface energy of coated corona-treated film reduced with time making it unsuitable for subsequent coating. Studies on the effect of corona treatment on such film might open a new vista of packaging technology.

3. Water-based coatings are known for their poor spreadability and adhesion characteristics due to the high surface energy of water. There is no study on the influence of corona treatment on such hydrophobic films, which might be undertaken.

4. In comparison to corona treatment the efficacy and feasibility study of plasma treatment may be of interest to future researchers in search of a paradigm shift in the packaging.

5. Another means of surface modification is by gamma radiation. Though it is a very fast process but a capital-intensive one. A comparative cost-benefit analysis along with its industrial suitability may be undertaken as a future dissertation.

6. In order to cater to the quality of the product before significant deterioration, the shelf life of packaging material is also important alongside the shelf life of the product itself. This area has always been ignored to a large extent. The effect of aging of the multilayered laminated structures till they become unusable at different storage conditions need detail investigation in order to specify the shelf life of the widely used flexible packaging materials in the industry.